3.2 First-Principles Calculation of Material Properties

Mechanisms of Semiconductor Interface Formation and its Electronic Properties based on Quantum Theory

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In the fiscal year of 2019, on the basis of the total-energy electronic-structure calculations and molecular dynamics simulations within the density-functional theory, we have studied atomscale behavior during the epitaxial growth of power semiconductors, silicon carbide (SiC) and gallium nitride (GaN). The main computa tional tools are our RSDFT (Real Space Density Functional Theory) code and RS-CPMD (Car-Parrinello Molecular Dynamics) code. We have clarified 1) the structures and energetics, and then the morphology of SiC surface steps [1,2], 2) the liquid-like behavior of the topmost Ga atoms [3] and 3) the mechanism of oxygen incorporation during the epitaxial growth of GaN [4,5]. The group identification codes for the achievements above are k0042 and m0001. Below, I explain the issues 1) and 2).

1. Step structures and morphology of Siface SiC Polar Surface

SiC is now emerging as a promising material for power electronics. This is due to its physical properties superior to Si, a current premier material, such as the wider band gap and the higher electric break-down voltage. The thin-film growth of SiC in the step-flow mode is essential

the fabrication of electronic devices. in Understanding of bond configurations near the step on the atomistic level is necessary in order to identify the reactivity at the step edges. Furthermore, epitaxial graphene can be prepared on SiC surfaces, and the surface steps of SiC also play an important role. Hence, it is certainly important and inevitable from both science and technology viewpoints to identify the atomic steps on SiC and clarify their energetics, that has not been achieved yet. Our previous calculations [6] show that the single-bilayer height steps are



Fig.1: Schematic view of the five distinct mono-bilayer steps on SiC (0001) surface. Si and C atoms are represented by the larger (blue) and smaller (brown) balls, respectively. The Si2, Si3, C1 and C2 steps along the $\langle 11-20 \rangle$ direction and the SC step along the $\langle 1-100 \rangle$ direction are shown all together.

energetically favorable compared with higher steps on SiC(0001) or (111) surface.

Figure 1 shows schematic view of 5 distinct single-bilayer height steps. There are two different classes of steps: One is [11-20] oriented and the other is the [1-100] oriented; further in the latter, four different step edges exit which are labelled by the atomic species at the edge and the number of the dangling bonds before the structural relaxation as Si2, Si3, C1 and C2.

We have performed detailed structural optimization for all the possible atomic steps and determined their structures. Near step edges we have found prominent rebonding between the upper-terrace and the lower terrace Si atoms in Si2 and SC steps and also a peculiar resonant-like rebonds for Si3 steps, as well as the C dimerization for the C2 step.

Figure 2 shows calculated formation energies



Fig. 2: Calculated formation energies of the mono-bilayer atomic steps on SiC(0001) surface as a function of the Si chemical potential μ_{Si} , measured from that in crystalline Si, $\mu_{Si(bulk)}$. Shaded areas surrounded by each pair of solid lines represent the uncertainty in the calculated formation energy.

for 5 distinct steps as a function of Si chemical potential (Near step edges, the numbers of Si and C atoms are different so that we need the chemical potential). We have found that Si2 step toward [1-100] is the most stable and Si3 step follows. The SC step toward [11-20] is comparable with the Si3 step.

The energetics obtained above predicts some interesting morphology of atomic steps on SiC(0001). Experimentally, the (0001) surface is slightly inclined along either [1-100] or [11-20] direction. When it is inclined along the [1-100], the surface consists of the [0001] terrace and several steps among Si2, Si3, C1 and C2, whereas it consists of the terrace and SC steps when inclined along [11-20]. In the former, the Si2 or Si3 steps are energetically favorable (Fig. 2). However, in the latter, the SC step is energetically unfavorable compared with Si2 and also Si3 in some range of the Si chemical potential. Hence we expect that the steps toward [11-20] show zigzag shape consisting of, for instance, Si2 and Si3. We have indeed found that such zizgzag-shaped step-edge pairs of Si2 +Si3 is lower in the formation energy than the straight-shape SC step on the [0001] surface inclined along [11-20] direction.

2. Two-Dimensional Ga liquid on growing GaN surface

GaN, a fundamental material worldwide used for high performing opto-electronic devices, is rapidly becoming another candidate to unseat Si in power electronics. Yet, their practical realization asks for the realization of thin epitaxial films of higher quality with respect to what is done nowadays for optoelectronic applications. It is thus highly demanded to clarify the nature of the growing GaN surface at atomistic level.

It is known that under typical conditions of the epitaxial growth of GaN, the surface is Ga-rich. Hence we prepare Ga-rich surface and raise the temperature by CPMD simulations from room temperature. We have found that, when the typical temperature reaches the growth temperature, i.e., 1300 K, the topmost Ga atom suddenly moves from their original position. The calculated Ga-Ga pair correlation function is shown in Fig. 3. At room temperature, the toplayer Ga atoms vibrate around their original positions. The pair correlation function shows a peak determined by the Ga coverage. Then with increasing temperature, the pair correlation function shows the peak at the same position with increasing peak width, showing the enhanced thermal vibration. However, at the growth



Fig. 3: Evolution of the Ga-Ga pair correlation function in the top-layer of GaN during the heating process. The initial distance of 6.4 Å corresponds to the relaxed system from which dynamical simulations were started.

temperature, the top-layer Ga atoms get together and exhibit the peak at much shorter distance, indicating some condensed phase of Ga.

By using Kubo-formula (velocity-velocity correlation function), we have computed the diffusion coefficient of the top-layer Ga atom. We have found that the diffusion coefficient jumps at 1300 K from its value of $0.382 \times 10^{-5} \text{ cm}^2/\text{s}$ at 1100 K to the value of $0.492 \times 10^{-4} \text{ cm}^2/\text{s}$. We thus conclude that this condensed phase is not a solid phase but a two-dimensional liquid phase. This is corroborated by the absence of the peaks except for the first peak at 1300 K in Fig. 3. The notion that the GaN surface during the epitaxial growth is 2-diemnsional liquid is unrecognized in the past and important to consider mechanism of the epitaxial growth.

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Analyses on electronic structure and magnetic property in high-performance spintronics and magnetic materials

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Magnetic anisotropy calculation.

We have developed a computational method of magnetic anisotropy energy (MAE) using the noncollinear spin density functional theory (NC-SDFT). This method enables us to estimate the MAE including both contributions to the MAE from magnetocrystalline anisotropy energy (MCAE) originating from spinorbit coupling and the shape magnetic anisotropy energy (SMAE) originating from spin dipole-dipole interaction [1]. In the calculation of SMAE, the contribution was estimated from the spin density distribution that is obtained in the NC-SDFT. One can expect an accurate SMAE. Indeed, we have found some corrections on SMAE coming from the quadrupole component of atomic spin density [2,3].

We applied the method to the freestanding Co/Ni(111) multilayer that indicates a perpendicular anisotropy [1]. The results indicated a good agreement with an available experimental measurement, as shown in Fig.1. This agreement implies that our method is promising on the estimation of MAE.

We have established a calculation method of MCAE in the same time. The MCAE part was evaluated from both methods of total energy (TE) and grandcanonical force theorem (GCFT) [1]. All MCAE values from the TE were well reproduced by those from the GCFT method. The advantage of GCFT method over the TE method makes analysis of the atom-resolved and k-resolved contributions of MCAE. In Fig.2, one can easily recognize the portions of large contribution to MCAE. Such figure can be compared with the orbital-resolved component of band dispersion curves. As a result, the MCAE is deeply understood, combined with its anisotropy of orbital components. The atom-revolved MCAE is also very useful to understand the atom/layer alignment giving rise to large



Fig. 1. MAE in Co/Ni multilayer structure as num. of multilayer.

MCAEs. In the application of Co/Ni(111), we recognized that the Co/Ni interface makes a large perpendicular magnetic anisotropy.

NC-SDFT under magnetic field.

We implemented a density functional scheme which enables application of a uniform external magnetic field. In the implementation, the rotation of the magnetic moment on an atom was described using the NC-SDFT calculation. The new scheme was successfully applied to a ferromagnetic slab with a perpendicular magnetic anisotropy and an antiferromagnetic material [4]. These results were discussed along with the simple model. This approach may provide a useful tool in analyzing magnetic properties of materials. In the scheme, the Kohn-Sham equation was solved self-consistently with the noncollinear spin density in the system.



Fig. 2 k-resolved MCAE in Co/Ni(111) multilayer structure.

Other contributions.

We have developed a noncollinear spin version of van der Waals density functional scheme [5]. We have also contributed a theoretical part of the spintronics application in the system of interfacial magnetic anisotropy of PtCoO/ZnO [6].

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Ab initio optimization of 4f-3d intermetallic ferromagnets for permanent magnets

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Today's main-stream commercial permanent magnets are made of sintered Nd-Fe-B alloys [1], or rapidly quenched alloys with analogous ingredients [2] that is fabricated into hotdeformed magnets. Their main-phase compound is a 4f-3d intermetallic ferromagnet, $Nd_2Fe_{14}B$ [3]. Its magnetization of 1.6 Tesla at room temperature and relatively good temperature dependence of anisotropy field [4] makes $Nd_2Fe_{14}B$ a champion magnet compound for practical applications in the temperature range from 300 K to 500 K, while its relatively low Curie temperature at 585 K, almost half of the Curie temperature of elemental Fe, leaves only a small temperature margin as compared to Sm-Co magnets whose Curie temperature reaches the range of 1000 K. The hightemperature properties that are not very excellent pose a drawback for the Nd-Fe-B alloy, leading to various proposals for alternative materials including $NdFe_{12}N$ [5, 6] and $SmFe_{12}$ [7], which cannot escape other problem concerning structure instability. In parallel with such quest for the possible next-generation champion magnets, it is important to better understand today's champion magnets and verify if there is any marginal space left for a possible improvement of R₂Fe₁₄B-based permanent magnets (R=rare earth). Thus we have been investigating optimally degined materi-

als with a pool of candidate chemical compositions, made of preferrably light rare earth elements and iron-group elements, where a good compromise involving all of the desired properties, such as structure stability, magnetization, magnetic anisotropy and Curie temperature, can be reached within a restricted lattice structure of $R_2T_{14}B$ (T=Fe or Co).

In order to explore the chemical composition space in a combinatorial way, we run massively parallel computer simulations for $R_2T_{14}B$ covering a virtual space spanned by R's and T's utilizing AkaiKKR [8], the opensource package for *ab initio* electronic structure calculations based on Korringa-Kohn-Rostoker (KKR) Green's function method implementing coherent potential approximation. Once a selfconsistent electronic structure is reached, an estimate of the Curie temperature can be done as a post-processing to the converged result, based on an approximation to consider the lowmost excitations on the Fermi level dominantly contributed from the ferromagnetic spin waves. Atomic-pair wise exchange couplings can be estimated based on a magnetic force theorem following Liechtenstein et al. [9] and a realistic Heisenberg model defined from them can be solved by the mean-field approximation. The working lattice constants are basically taken from past experiments [3].



Figure 1: Calculated Curie temperature of $R_2Fe_{14}B$ (red squqre) based on muffin-tin approximation (MTA). For a comparison, the experimental data (blue circle) taken from Ref. [3] are also shown.

Calculated Curie temperature in a representative cross section of the overall chemical composition space, (R,T), are shown in Fig. 1. Here we show the computational data set based on local density approximation [10] and within muffin-tin approximation. An analogous and more comprehensive data set within atomic-sphere approximation is published elsewhere [11]. It is seen that the overall trend with respect to the species of rare-earth elements is described satisfactorily, while the quantitative accuracy is not as excellent. The systematic deviation is reasonable, considering one of the biggest approximations we have made in modeling a metallic system only with spin degrees of freedom, as if our target systems were insulators. On top of that, temperature dependence of lattice constants would not entirely be negligible under the strong influence of the magnetovolume effect in such a strong ferromagnet [12]. Since the Curie temperature is mostly contributed from 3delectrons, the relative trend within a materials family where the 3*d*-electron part is common seems to be well described. As long as we are aware of the particular way the systematic deviation between theory and experiment comes in, it is expected that we can carefully utilize the data obtained within the prohibitively crude approximation based on spin models even for intermetallics.

More extensive data collections to elucidate the overall trends have been in progress and will be published elsewhere.

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Data integration between theory and experiment for rare-earth permanent magnets

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Materials in practical use are characterized with macroscopic properties in a space-time scale comparable to the human scale, as rareearth permanent magnets are with remanent magnetization and coercivity that works in operation environments that are typically out of thermal equilibrium. It is desirable to have a working methodology to understand and control those macroscopic properties of materials from the fundamental laws for atoms and molecules.

We have been in quest for such materials design scheme spanning over the microscopic and macroscopic physics. We have recently constructed an iterative approach between experimental data and theoretical data, taking as our playground a material of recent interest, namely, $SmFe_{12}$ with substitution elements such as Ti, Co, and Zr, a candidate material for a new permanent magnet. Effects of Ti, Co, and Zr for multiple prerequisite properties for permanent magnet utilities, put in multiple sublattices, are investigated utilizing both of *ab initio* theoretical data and experimental data from neutron diffraction. Going back and forth between the Rietveld analysis for the latter and *ab initio* calculations based on local density approximation (LDA) until a fixed point is reached, dual site preference of Zr in $SmFe_{12}$ has been newly elucidated, in contrast to the prevailing assumption in the literature that Zr replaces Sm only. This way of data-integration analysis has been tentatively called "LDA+Rietveld" method [1], as has been constructed in an analogous spirit to LDA+DMFT (DMFT =dynamical mean field theory) [2].

For LDA+Rietveld, we have utilized AkaiKKR [3] for incorporating the substitute elements with a continuous variables of the concentration. *OpenMX* [4] is needed as well in order to address the structure stability with calculated formation energy. In LDA+DMFT, LmtART [5] has been utilized combined with a continuous-time quantum Monte Carlo impurity solver adapted for our realistic simulations.

Taking LDA+DMFT as a prototype, we have made one step forward in constructing a working simulation framework to bridge over the microscopic scale and the macroscopic scale.

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Physics of Electrochemical Interfaces

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The metal-solution interface exhibits various properties under the influence of the electrical double layer formed around the interface. Our group has been elucidating the reaction dynamics and adsorption processes from microscopic а perspective using interface-adapted first-principles computational methods. This year, our lab focuses on the following two different themes: (A) the quantum nuclear effect of hydrogen adsorption at the Pt(111)-solution interface [1] and (B) the role of defects in the activation of oxygen reduction reactions at the TiO_2 -solution interface [2].

(A) Hydrogen atoms are known to exhibit large quantum effects, but these effects have been investigated only at the full mono-layer coverage $(\theta = 1)$ or the low coverage limit ($\theta \ll$ 1). In the former, hydrogen is recognized as a classical particle modified by the zero-point energy, and in the latter, hydrogen is recognized \mathbf{as} а quantum mechanically extended particle; our first-principles path-integral simulations for $\theta = 2/3$ and 1 capture the crossover, which can be explained by a lattice gas model with a quantum hopping term, or the Boson-Hubbard model. The results provide new insights into the mechanism of the hydrogen evolution reaction.

(B) Defective TiO_2 has been recognized as a future material for hydrogen fuel cell catalysts because of coexistence of the stability and activity, but the mechanism of the oxygen reduction reaction (ORR) is unknown. To search for the active site of this material, we took a highthroughput approach based on thermodynamics. Since important key to the activity is in the relative stability of the reaction intermediates, O OH. and we investigated how one can control the stability by doping. Contrary to many materials like platinum, TiO₂ surfaces were found to bond O and OH differently when doped differently, suggesting it possible to sufficiently flatten the potential for energy profile ORR. This discovery has stimulated experimental collaborators to design

a novel fuel cell.

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DFT sampling analysis on interfaces and electrolytes in novel batteries

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We are working on (1) developments of theoretical, computational and data-driven techniques [1,2] as well as (2) understanding of surface and interface reactions, essential in the energy and environmental technologies such as battery and catalyst [3-8]. Recently, we have made a progress for DFT-based efficient calculations of solid-solid interfaces, mainly for all-solid-state batteries [1].

We have been exploring the atomistic understanding of this interfacial resistance mechanism with DFT-based calculations [4]. We first devised some systematic ways for the solid-solid interfaces and discussed possible origins such as the space-charge layer and the reaction layer. Recently, we incorporated the CALYPSO structure prediction technique with our method for the interface structure search, including mismatch treatment and lateral shift etc [1]. In this way, we have found several microscopic electrochemistry of the interfacial Li-ion states.

As a representative model, we investigated the system with LiCoO₂ (LCO), β -Li₃PS₄ (LPS), and LiNbO₃ (LNO) acting as a cathode, a sulfide electrolyte, and a buffer layer, respectively. For the LCO/LPS interfaces, we sampled over 20000 configurations and found several stable disordered structures involving mixing cations and anions, leading to the formation of a reaction layer. On the other hand, Li-ion sites that can be preferentially depleted upon charging always exist around the cathode-SE interfaces irrespective of the interfacial order/disorder (See Li Chemical potential in Figure). Therefore, we conclude that the dynamic Li-ion depletion is likely to be a major cause that prevents successive Li-ion transport, leading to resistance.



Fig. 1 Li chemical potentials around an interface between $LiCoO_2$ cathode and β -Li₃PS₄ solid electrolyte; Pristine interface (left) and Co-P exchange interface (right).

Through investigating the buffer layer effects and the interfacial electronic states, we also deduced a probable origin for the interfacial Li depletion and a mean to suppress this problematic behavior.

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Theoretical study on defects in wide-gap semiconductors: SiC and α -Ga₂O₃

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We have studied the stabilities of defects in wide-gap semiconductors on the basis of the density-functional theory (DFT). In this study, we focus on SiC and α -Ga₂O₃ as nextgeneration of power semiconducting materials. To clarify the stable defect structures and its electronic properties is necessary to move the power device applications forwards.

First, we have discussed the energetics of carbon-related defects in the SiC, SiO₂, and just at their interface for the systematic comparison of the stabilities of them in the three regions. As a result, we have found that the stable forms of the carbon defects depend on the oxidation environment. In the oxygen-rich condition at 1600K, nano carbon clusters likely to stay just at the SiC/SiO₂ interfaces [1]. According to the calculations, a high temperature oxygen-poor condition is preferable for reducing the remained carbon defects near the interface.

Very recently, an EDMR experiment detected carbon-dangling bonds along the direction perpendicular to the interface. We succeeded in identifying the atomic structure of the defect as an ad-atom with a dangling bond $(P_{\rm b} \text{ center})$ based on the DFT calculations [2].

We have also calculated the formation energies of point defects in α -Ga₂O₃ [3]. We have used the extended FNV method to remove the artifacts derived from the background charge. We have found that Ga interstitials and Ga vacancies are the major defects when the Fermi energy approaches to valence and conduction bands, respectively.

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First-principles configurational sampling of highly-doped ionic conductors

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Ceramic-based electrolytes under are intense research for application in battery, fuel cell, and electrolyzer applications. These materials are usually prepared by doping insulating materials. When the chargecompensating defect is the hole or electron, you have a semiconductor. When the compensating defect is a mobile ion (or ion vacancy), you obtain an ionic conductor. Often, these materials are used at rather high dopant percentages of up to $\sim 30\%$ where the conductivity is maximized. There is still much to what determines controversy as this maximum, and computer simulations are expected to help in this regard.

At such high dopant concentrations, the short to middle-range order of the dopant arrangements should have a profound effect on the conductivity. To simulate this, i.e., dopant arrangements as functions of temperature and dopant content, we combined the replica exchange Monte Carlo method directly with DFT calculations [1] (the software for achieving this was selected as this year's Software Advancement Project, so details can be found in that section). For example, Figure 1 shows the percolation of dopants in Y-doped BaZrO₃ vs. temperature calculated for several dopant concentrations. A profound temperature dependence is seen at 15%, which is close to the percolation threshold. Further discussion including successful reproduction of the dopant concentration for maximum conductivity can be found in Ref. [2].



Figure 1 Percolation as functions of temperature for dopant ratios of 7, 15, 22, and 30 mol% in Y-doped BaZrO₃.

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Analyses of Atomic Structures and Atom Dynamics at Surfaces, Interfaces and Defects

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1 Introduction

The understanding on atomic structures and atom dynamics at surfaces, interfaces and defects is crucial to facilitate innovation of novel nanoscale information and energy devices. First-principles calculation is a powerful tool to obtain such understanding, but still insufficient to tackle with complex models corresponding to real devices.

Keeping the above in minds, we have been investigating atomic structures and atom dynamics in various systems via first-principles calculations combined with multi-scale or machine-learning approaches. In the followings, some of our results in the fiscal year 2018 are described.

2 Structure of interfaces between metal and solid electrolyte

The distribution and dynamics of Li ions near the interfaces between metal electrode and solid electrolyte play important roles in the operation mechanisms of novel memory device named VOLRAM [1] and all-solid-state Li-ion batteries. We examined Li ion distribution at the interfaces between γ -Li₃PO₄ and metal electrodes by the method [2] combining first-principles data of defect formation energies with a one-dimensional continuum model.

Our results [3] show that within the allowed range of the chemical potential of Li in γ -Li₃PO₄, upward band bending occurs near Au(111) and Ni(111) interfaces. This upward bending is caused by the accumulation of interstitial Li-ions at the metal-Li₃PO₄ interfaces, and the thickness of the Li-ion accumulation layer is the order of a few Å. For the Li(100) interface, the band bending behavior depends on the chemical potential of Li, $\mu_{\rm Li}$: Slight upward bending occurs for $\mu_{\rm Li} = -2.59$ eV, while downward bending occurs for $\mu_{\rm Li} = -6.11$ eV owing to the accumulation of Li vacancies.

Since Au and Li are known to form alloys, we also performed simulations taking account of the alloy formation in the form of work function change. Figure 1 shows the calculated electrostatic potentials and interstitial Li distribution profiles in γ -Li₃PO₄ with Au(111), LiAu₃ and Li₃Au(100). In all cases, the potential profiles show upward bending and the accumulation of interstitial Li ions near the interfaces. However, the amount of interstitial Li-ions decreases for the alloy cases. From this result, we can explain the switching of VOL-RAM.

3 Phonon-related properties of GaN

Conisdering the facts that GaN is promising for power semiconductor device and thermal management is important in power semiconductor device, we have been examining phonon band structures and thermal transport properties of GaN. In the fiscal year 2018, we had constructed the high-dimensional neural network potential (HDNNP) [4] for crystalline GaN, and calculated the phonon band structures and thermal conductivities using the



Figure 1: Calculated electrostatic potential and the interstitial Li fraction profiles of γ -Li₃PO₄ as a function of the distance from the interface z, with Au(111), LiAu₃(111), and Li₃Au(100) (reproduced from Ref. [3]). The reference of the electrostatic potential corresponds to the Fermi level of metal surfaces. The chemical potential of Li is set to -2.59 eV.

constructed HDNNP. Our preliminary results were described in the Activity Report 2018.

In the fiscal year 2019, we improved the HDNNP and examined the phonon band structures and thermal conductivities more closely [5]. To obtain data of atomic structures, energies and forces, we performed classical molecular dynamics (MD) simulations with a well-established interatomic potential and then evaluated the energies and forces by the density functional theory (DFT) for structures sampled from the trajectories of classical MD. The final root mean square errors of force and total energy prediction in the validation data were 37.8 meV Å⁻¹ and 66.5 meV atom⁻¹, respectively. The lattice thermal conductivity were calculated based on anharmonic lattice

dynamics using the phono3py package. The calculation results from HDNNP and DFT under the same simulation conditions are in good agreement, indicating the strong potential of HDNNP for application in thermal conductivity simulations: The deviation from the DFT calculation results is within 5.4% from 200 to 1000 K.

Then we constructed HDNNP for GaN crystal with N vacancies, and calculated the phonon band structures and thermal conductivities of GaN with N vacancies. In our preliminary calculations, we obtained reasonable phonon energy bands and thermal conductivities. We will check the reliability of the HDNNP and examine the effects of N vacancy on the phonon band and thermal conductivity in moe detail in the fiscal year 2020.

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First-principles molecular dynamics simulation of the water/air interface using hybrid functionals

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Density functional theory-based molecular dynamics simulations are increasingly being used for simulating aqueous interfaces. Nonetheless, the choice of the appropriate density functional, critically affecting the outcome of the simulation, has remained arbitrary. Here, we assess the performance of various exchange-correlation (XC) functionals, based on the metrics relevant to sum-frequency generation spectroscopy. The structure and dynamics of water at the water-air interface are governed by heterogeneous intermolecular interactions, therefore providing a critical benchmark for XC functionals. We find that the revPBE and revPBE0 with the dispersion correction show excellent performance. The poor performance of the empirically optimized density-functional (M06-L) manifests the importance of satisfying exact functional condition. Understanding the performance of different XC functionals can aid resolving the controversial interpretation of the interfacial water structure and direct the design of novel, improved XC functionals better suited to describe the heterogeneous interactions in

condensed phases. [1]

We employed the CP2K code [2], which is based on the mixed Gaussian and plane wave basis sets.



Fig. 1: The ability of different functionals to accurately predict water properties is directly compared. The smaller (larger) score κ corresponds to better (worse) predictive power of the functional [1].

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First-principles molecular dynamics simulation of electrondoped graphene/water interfaces

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Ab initio molecular dynamics (AIMD) simulation is a powerful tool to describe heterogeneous systems such as the water/solid interface. Although AIMD is computationally expensive, it describes electronic states beyond classical force fields,[1] which is important for interfaces.

We have simulated sum-frequency generation (SFG) spectra of isotopically diluted water at the water-graphene and water-hexagonal boronnitride (hBN) sheet interfaces, using ab initio molecular dynamics simulations. The simulations themselves were performed using ISSP several years ago and recently the paper was published.[2] A sharp 'dangling' O-D peak around ~2640 cm-1 appearing in both simulated SFG spectra evidences that both graphene and hBN are hydrophobic. The dangling O-D peak is 10 cm⁻¹ red-shifted at the water-hBN interface relative to the peak at the water-graphene interfaces. This frequency difference manifests a stronger O-D...N intermolecular interaction between water and hBN than a O-D...C interaction between water and graphene.

To modify the hydrophobic interaction, we calculated electron-doped-graphene water interfaces using the CP2K code [3]. Although I got preliminary results, it seems that the integer number of electrons is too strong electron doping. It will be required to think about using plane wave codes (though they are computationally demanding).



Fig. 1: Structures of the graphene-water interface.

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Development of first-principles electronic-structure and transport calculation code RSPACE and simulations for device

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Silicon carbide (SiC) has attracted considerable attention owing to its excellent physical properties, such as its high thermal conductivity, high breakdown strength, and large band gap. It is also advantageous that the oxidation of SiC leads to SiO_2 , since it is well known that SiO_2 exhibits good dielectric properties in Si device technology. However, unlike Si MOSFETs, SiC MOSFETs have unacceptably low carrier mobility. One of the origins of the low carrier mobility is the generation of a large number of interface defects at the SiC/SiO2 interface during the thermal oxidation. In this study, we carried out density functional theory calculations to examine the oxidation process of $SiC(0001)/SiO_2$ interfaces showin in Fig. 1.[2]

It is not straightforward to characterize the atomic structure of the $SiC(0001)/SiO_2$ interface because SiO_2 at the SiC/SiO_2 interface is mainly amorphous. Here, I assume that crystalline structures exist locally at the SiC/SiO_2 interface and employ the most possible candidate for the interface atomic structures reported in Ref. 2. RSPACE code[4] is used for the first-principles calculations. The energy barriers in the oxidation process are computed by the nudged elastic band method. The lateral lengths of the supercell are chosen to be $\sqrt{3a}$ and 3a along the $[1\overline{1}00]$ and $[11\overline{2}0]$ directions of the 4H-SiC(0001) surface, where ais the lattice constant of SiC, and integration over the Brillouin zone is carried out using a 2 \times 3 \vec{k} -point mesh.

The oxidation of 4H-SiC is assumed to proceed by the process which we proposed in the previous study: [3] (a) an O₂ molecule arrives at the interface, splits, and cuts into the Si-C bonds (2O_{if}). (b) One of the O atoms among the Si-C bonds migrates to a site between the Si and C atoms connecting the first and second SiC bilayers $(O_{sub}+O_{if})$. (c) the third O atom comes by migration between the SiC bonds $(O_{sub}+2O_{if})$ (d) Due to the interface lattice mismatch, CO molecule detachment occurs at the interface $(2O_{if}V_{C}+CO)$. I found that the largest energy barrier is 3.21 eV for process (a). Gavrikov et al. [5] employed the interface model, where two- and three-fold structures are mixed, and reported that the activation barrier is larger than 3.5 eV, which is required for the penetration of an O_2 molecule through the interfacial layer of SiO_2 . It is reported by Shen *et al.* [6] that the barrier for an O_2 molecule penetration is ~ 4.0 eV. Akiyama *et al.* [7] reported the activation barrier of 3.2 eV using the computational model similar to the 4H-SiC(0001)/ β -tridymite SiO₂. Their reaction path resembles the atomic oxygen mechanism, in which O atoms diffuse by hopping from one bond to another, rather than an O_2 molecule penetration. Shen *et al.* also reported that the barrier for the atomic oxygen mechanism is ~ 3.1 eV. Although my reaction process (a) is similar to that proposed by Akiyama *et al.*, in which the O_2 molecule is not a molecule after passing the interfacial SiO_2 layer, my process is different from their situation, in which the interfacial O atom hops to the SiC bond and Si₂-CO structure is generated. When I assume that the O₂ molecule behaves like two O atoms at the oxidation front, the activation barriers obtained by these theoretical calculations are comparable. Thus, O₂ molecules dissociate when they pass the interfacial SiO₂ layer with the barrier of ~ 3.2 eV.

Next, let me discuss the barrier after the O atoms cut into the SiC bonds. Gavrikov et al. reported that the CO molecule is emitted from the Si_2 -CO structure with the activation barrier of 2.8 eV. Since the Si₂-CO structure is less stable than the $O_{sub}+O_{if}$ structure by 0.6 eV, the total activation barrier from the O_{sub}+O_{if} structure is 3.4 eV. Köhler *et al.* reported the barrier for the CO molecule detachment of 3.1 eV. If the energy difference reported by Gavrikov et al. is added, the total barrier from the $O_{sub}+O_{if}$ structure is 3.7 eV. It is also reported by Akiyama *et al.* that the activation barrier for the CO molecule detachment from the Si_2 -CO structure is 1.7 eV, which is much smaller than the results calculated by Gavrikov et al. and Köhler et al. If I believe the larger barrier calculated by Gavrikov et al. and Köhler et al., these results imply that the CO detachment also limits the reaction. However, in our previous study [3], we reported that the CO desorption preferentially occurs when the interfacial C atom is surrounded by three O atoms. The activation barriers for the migration of O atoms at the SiC/SiO_2 interface are 2.72 eV for process (b) and 2.08 eV for process (c). It is noteworthy that these barriers vary between 2.0 eV and 2.8 eV depending on the configuration of the O atoms at the interface. When the third O atom is considered, the barrier for the O_2 molecule penetration is still higher than that for the CO detachment. Thus, it can be concluded that the CO detachment does not limit the reaction and the O_2 molecule penetration

is the reaction-limiting process.



Figure 1: Interface atomic structure of β tridymite SiO₂ on SiC. Blue, brown, and red balls are Si, C, and O atoms, respectively. The supercell contains 30 Si, 24 C, 14 O, and 8 H atoms. H atoms are used for termination of dangling bonds at the surfaces.

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First-Principles Study of Excited Electron, Positron and Atom Dynamics and Optical and Thermoelectric Properties of Nanostructures

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In this project we investigated the following four topics on the basis of time-dependent density functional theory (TDDFT). 1) Angleresolved photoemission spectroscopy (ARPES) in low-dimensional periodic structures, 2) Stationary-state electron scattering using a complex injecting potential (CIP), 3) Optical and thermoelectric properties of low dimensional materials, and 4) Development of the exchange-correlation term in TDDFT.

1) Angle-resolved photoemission spectroscopy in low-dimensional periodic structures [1]:

We proposed a new approach based on TDDFT for the calculation of ARPES of low-dimensional periodic structures, such as graphene, silicene, and polyacetylene. The calculated ARPES spectra reproduced the occupied energy band structures fairly well. We further investigate the electron doping effect on ARPES by considering Li-intercalated bilayer graphene and found a shift in the Fermi energy. These show that the present method can provide reliable ARPES spectra for materials for which ARPES experiments are difficult to perform under some conditions. We note that the present method is simpler and uses a more direct one-shot TDDFT calculation for ARPES than previous theories. Further applications to time-resolved and spin-resolved ARPES simulations will be presented elsewhere. The simulations have been conducted by our homemade TDDFT code,

KENS. Parallelized calculations have been performed using System B.

2) Stationary-state electron scattering using a complex injecting potential [2]:

We simulated stationary electron scattering by solving the time-dependent Schrödinger equation with a CIP. The calculated electron transmission probabilities through onedimensional potentials and the electron interference patterns caused by double slits show good agreement with analytical results. The Aharonov–Bohm effect is also clearly demonstrated by the presence of a vector potential at one side of the double-slit configuration. Also, from the simulation of the arranged-CIP method, we predict that this new method can be applied to BEC interference simulations. Since the present method can be straightforwardly extended to TDDFT, we can simulate field electron emission, photo-induced electron emission, secondary electron emission, thermionic emission, and so on. The simulations have been conducted by our homemade code, SCIP, using System B.

3) Optical and thermoelectric properties of low dimensional materials [3]:

We studied the optical and thermoelectric properties of various low dimensional materials by means of the first-principles method.

First, we applied TDDFT to the calculation of absorption spectra for two-dimensional atomic-layer materials: mono-layer and bilayer hexagonal boron nitride (h-BN) and mono-layer transition metal dichalcogenides, MoS_2 and $MoSe_2$. We demonstrated that the TDDFT approach with the meta GGA exchange-correlation potential and the bootstrap kernel can capture the characteristics of the first bright excitonic peak of bi-layer h-BN that is dependent on the layer stacking type. We also revealed that the TDDFT method can capture the qualitative features of the absorption spectra for mono-layer transition metal dichalcogenides, although the exciton binding energies are underestimated compared to those obtained by the many-body pertubation theory (MBPT) calculation. This study elucidates the usefulness of the TDDFT approach for the qualitative investigation of the optical properties of two-dimensional atomic layer materials. MBPT calculations and TDDFT calculations have been conduced using EXCITING (http://exciting-code.org/) and ELK (http://elk.sourceforge.net/) code, Parallelized calculations have respectively. been performed using System B.

Next, we calculated the thermoelectric power factor of pnictogen (P, As, Sb, Bi) nanoribbon structures using the density functional theory (DFT) and non-equilibrium Green's function (NEGF) method. We found that the power factor properties strongly depend on the structure of nanoribbons, i.e., the buckled nanoribbon generally exhibit higher power factor than the puckered one. It was also found that the light pnictogens (P, As, Sb) have an advantage over the heavy one (Bi) in giving a high power factor. This study reveals a part of the relationship between the electronic structure and the thermoelectric property of pnictogen nanoribbons, and provides the useful information to develop the thermoelectric devices based on pnictogen nanoribbons. All DFT calculations and NEGF calculations have been conduced using Quantum Espresso (https://www.quantum-espresso.org/) and WanT (http://www.wannier-transport.org/) code, respectively. Parallelized calculations have been performed using System B. 4)Development of the exchange-correlation term in TDDFT:

We developed a machine learning based approach to improve the approximation to the exchange-correlation potential of TDDFT. We trained the neural-network projection from the time-varying electron densities to the corresponding correlation potentials in the time dependent Kohn-Sham equation using a few exact datasets for a model system of electronhydrogen scattering. We demonstrated that this neural-network potential can capture the complex structures in the time-dependent correlation potential during the scattering process and provide correct scattering probabilities, which are not obtained by the standard adiabatic functionals. This study offers a novel way to improve the exchange-correlation potential of TDDFT. The simulations have been conducted by our homemade code. Parallelized calculations have been performed using System B.

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Ab initio phonon calculation for $Ca_5Ir_3O_{12}$

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The title compound has recently attracted attention as a thermoelectric material because it has a relatively high Seebeck coefficient. In this study, we report an ab initio study about electronic and phononic properties for $Ca_5Ir_3O_{12}$. In particular, we investigated the effect of spin-orbit interaction (SOI) on the low-energy properties [1].

Density functional calculations with planewave basis sets were performed using the xTAPP code [2], where the ultrasoft pseudopotential and the generalized gradient approximation (GGA) of the exchange correlation potential were employed. The cutoff energies in the wavefunction and charge densities were 64 and 900 Ry, respectively, and the SOI was explicitly considered. To study the effects of SOI, we performed the usual GGA calculation and compared it with the result including the SOI. Below, we refer to the former as GGA and to the latter as SO-GGA. The atomic and lattice parameters were optimized with an $8 \times 8 \times 8$ kpoint sampling, and we found that SO-GGA reproduces the experimental crystal structure quite well. The Fermi-surface calculations were performed with the dense $21 \times 21 \times 63$ kpoint sampling to obtain the detailed surface structure [3]. Phonon calculations with a frozen phonon approximation were performed using the PHONOPY for $1 \times 1 \times 3$ and $2 \times 2 \times 1$ supercells [5, 6]. For the k-point sampling, $11 \times 11 \times 11$ was used for $1 \times 1 \times 3$ supercell calculation, and somewhat coarse $9 \times 9 \times 5$ was used for the $2 \times 2 \times 1$ supercell calculation.

Figure 1(a) shows our calculated band structure. To see the SOI effect, the SO-GGA band



Figure 1: (Color online) (a) Ab initio electronic band structure considering the SOI in $Ca_5Ir_3O_{12}$. The energy zero is the Fermi level. (b) A zoom of the low-energy band structure, where the SO-GGA result (thick red curves) is compared with the usual GGA result (thin blue curve). (c) Calculated Fermi surface for SO-GGA and (d) GGA.

(thick red curves) is compared with the GGA band (thin blue curves) in Fig. 1(b). An appreciable difference can be observed in the lowenergy bands; the GGA result exhibits metallic bands, particularly along the L-M or H-K lines. When the SOI is switched on, the metallic bands are split and a pocket-like band structure appears. The gap size due to the SOI is about 0.3 eV, which is comparable to the valence bandwidth 0.5 eV.

Figures 1(c) and 1(d) show the Fermi surfaces based on the SO-GGA and GGA, respectively. We see that the GGA Fermi surface is contributed from the two bands (indicated in dark-blue and bright-red colors), while the SO-GGA Fermi surface is basically formed by the one band; the SOI makes the bright-red colored GGA Fermi surface disappear. In the SO-GGA Fermi surface, since the SOI resolves the band degeneracy, the Fermi surfaces are seemingly two (dark-blue and bright-blue colored surfaces); however, these two are originated from the same band. Also, in the SO-GGA Fermi surface, we see a sheet structure along the c^{*}-axis (the Γ -A line), which indicates a nesting trend along this direction. We note that the SOI is relevant to the narrowing of the sheet separation between the blue colored Fermi surfaces.

Figures 2(a) and 2(b) are our calculated phonon dispersions with SOI for $1 \times 1 \times 3$ and $2 \times 2 \times 1$ supercells, respectively. It was found that the experimental results at the room temperature are better reproduced by the $1 \times 1 \times 3$ supercell calculation. The panel (b) is a preliminary phonon calculation on a $2 \times 2 \times 1$ supercell. This supercell includes the displacement degree of freedom in an in-plane 2×2 superlattice, and we can investigate the phonon instability within this superlattice. On the other hand, the $1 \times 1 \times 3$ supercell can clarify the triple-period phonon instability along the *c*-axis. Within these two supercells, we observe phonon softening in the $2 \times 2 \times 1$ supercell calculation; there is a sign of softening at the K and

M points. However, since the calculation conditions for the $2 \times 2 \times 1$ calculation are rough, it is necessary to perform the calculation under more severe conditions.



Figure 2: (Color online) Ab initio phonon dispersion with the SOI in $Ca_5Ir_3O_{12}$. Panels (a) and (b) show results based on $1 \times 1 \times 3$ and $2 \times 2 \times 1$ superlattice, respectively.

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Ab initio derivation of effective low-energy model of $Ca_5Ir_3O_{12}$

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In this report, we report a first-principles derivation of an effective low-energy model for $Ca_5Ir_3O_{12}$. In order to perform the effectivemodel derivation of materials with strong spinorbit interaction (SOI) such as iridium system, we extended the first principle effective-model derivation software RESPACK [1] to the spinor type.

The density-functional band-structure calculations for $Ca_5Ir_3O_{12}$ are performed using xTAPP [2] with the experimental lattice parameters [3]: a = 9.3490 Å and c = 3.1713We use the norm-conserving pseudopo-Å. tential and the generalized gradient approximation (GGA) of the exchange correlation potential. We use $8 \times 8 \times 8$ k-points for sampling in the first Brillouin zone. The energy cutoff is set to be 144 Ry for the wave functions, and 576 Ry for the charge density. The interaction parameters are calculated using the constrained random-phase approximation method, in which we employ the scheme for the band disentanglement. The energy cutoff for the dielectric function is set to be 20 Ry. The total number of bands used in the calculation of the polarization is 300, which includes the unoccupied states up to $\sim 26 \text{ eV}$ with respect to the Fermi level. To study the effects of SOI, we performed the usual GGA calculation and compared it with the result including the SOI. Below, we refer to the former as GGA and to the latter as SO-GGA.

From the fat band analysis, it was found that the band structure near the Fermi energy is d_{xy} and d_{yz} orbitals. Here, the notation of the orbital follows a local coordinate system fixed to the IrO_6 octahedron. Based on this observation, we perform parameter derivation of the d_{xy}/d_{yz} model. Figure 1 is a comparison of the Wannier-interpolation band (greendashed curves) and the original band (red-solid curves). We see that the original band has been completely reproduced. Note that the initial guess setting is very important for obtaining such reproducibility. We set the d_{xy} and d_{yz} orbitals as initial guesses, where the initial guess orbitals are represented in the local coordinate system fixed to IrO_6 octahedrons, and additionally rotated the spin quantization axis. This treatment is very important to satisfy the symmetry of the calculated Wannier orbitals, that is, all 12 Wannier orbitals have the same spread.



Figure 1: (a) Ab initio density functional band structure considering the spin-orbit interaction in $Ca_5Ir_3O_{12}$.

We next show in Fig. 2 the resulting maximally localized Wannier functions for d_{xy}/d_{yz} model. The panels (a) and (b) indicate the d_{xy} and d_{yz} Wannier functions, respectively. Note that in this plot, three independent Wannier functions are shown in one panel.



Figure 2: Maximally localized Wannier functions of Ca₅Ir₃O₁₂: (a) d_{xy} and (b) d_{yz} Wannier functions.

Our derived model parameters for $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ are summarized in the Table 1. The spin-orbit coupling is estimated as 0.213 eV. The nearest neighbor parameter t_{NN} is 0.167 eV, the onsite interaction U based on constraind RPA is 2.43 eV, and the nearest-neighbor interaction V is estimated as 0.99 eV. Then, the correlation degree of freedom (U - V)/t is 8.62. Table 1: Main parameters of d_{xy}/d_{yz} model of Ca₅Ir₃O₁₂, where we show 3 nearest-neighbor (NN) transfers, onsite transfers, and largest interchain electron transfer. $t_{xy\uparrow,yz\uparrow}^{NN}$ and $t_{yz\uparrow,xy\uparrow}^{NN}$ are nearest neighbor transfers. Also, t_{onsite}^{onsite} is the spin-orbital couplings in the same site. The interaction parameters with the bare (unscreened) and constrained RPA (cRPA) are listed. $V_{\rm NN}$ is the orbital-averaged value of the nearest-neighbor interactions. Also, $V_{\rm IC}$ is the orbital-averaged value of the interchaicn interaction. The unit of the parameters is eV.

	SO-GGA		GGA	
$t_{xy\uparrow,yz\uparrow}^{\ \ NN}$	0.167		0.167	
$t_{yz\uparrow,xy\uparrow}^{\ \ NN}$	0.210		0.208	
$t_{interchain}^{\ largest}$	0.032		0.039	
$t_{xy\uparrow,yz\downarrow}^{onsite}$	0.213		-	
	bare	cRPA	bare	cRPA
U	9.87	2.43	10.03	2.23
U'	9.19	1.95	9.28	1.68
V_{NN}	4.43	0.99	4.39	0.77
$V_{interchain}$	2.86	0.52	2.86	0.44
J	0.27	0.21	0.29	0.23

As another achievement, we calculated the Raman frequency [4] and the phonon dispersion curves [5].

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First-principles calculations of thermoelectric properties in magnetic materials

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1. Development of Methods and Codes

The thermoelectric conversion based on the anomalous Nernst effect (ANE) has attracted much attention because the ANE realizes the high-density integration more easily compared to that based on the Seebeck effect [1]. The ANE is the phenomenon that the electric power is created along the direction perpendicular to both the temperature gradient and the magnetization in magnetic materials. This effect is induced by the anomalous Hall conductivity (AHC), and if the AHC changes drastically as a function of the Fermi level, we expect the large ANE[2]. In our previous firstprinciples study, we predicted that an electron doped EuO skyrmion crystal shows the large ANE induced by the finite Chern number at the Fermi level[3]. For discovery and design of new materials which have the large ANE via computational high throughput screening, we need an efficient computational method to investigate the Fermi level dependence of the AHC. We have implemented the code of computing the AHC applicable to metallic systems in OpenMX package^[4] by improving Fukui-Hatsugai-Suzuki method[5]. Using this code, we computed AHCs $\sigma_{xy}(\varepsilon)$ and transverse thermoelectric conductivities $\alpha_{xy}(\varepsilon)$ in two-dimensional ferromagnetic materials.

2. Applications to 2D Materials

The discovery of magnetism in the twodimensional materials[6] open a way for realizing thermoelectric devices based on anomalous Nernst effect. The surface phonon scattering advantage in the two-dimensional materials can decrease the thermal conductivity which can increase the thermoelectric figure of merit ZT[7]. The magnitude of anomalous Nernst effect itself depend on Seebeck effect or anomalous Hall effect [2, 3]. In our previous study, we reported that the half-metallic materials possess large anomalous Nernst effect[8]. Here, we performed first-principles calculations to explore the anomalous Nernst effect of half-metallic transition-metal dihalides monolayer using OpenMX package[4]. We analyzed its magnitude based on the semiclassical transport theory and found that there is large anomalous Nernst effect at 100 K. The large Berry curvature which contributed by bands near Fermi level is the main reason of its large magnitude. These results suggest that transition-metal dihalides monolayer can potentially be used in thermoelectric devices.

3. Thermal Conductivity and ZT

To evaluate efficiency of thermoelectric materials, it is important to examine the contribution of thermal conductivity to the thermoelectric figure of merit ZT that represents the performance of the material. Since the thermal conductivity can be described for each electron and lattice, in this research, we theoretically computed both electronic and lattice thermal conductivity, and then evaluated ZT. Theoretical analysis of lattice thermal conductivity is conducted by Boltzmann transport the-

ory with relaxation time approximation. In order to do this, it is necessary to determine the inharmonic atomic force constant exactly, and an accurate analysis is carried out by first-principles calculations based on density functional theory. As computational codes, OpenMX package[4] is used as a density functional calculation, and ALAMODE[9, 10] is used as a lattice thermal conductivity calculation. The half-Heusler compounds are ternary compounds, have composition formula of XYZ, and are expected as thermoelectric materials that exhibit high power factor in a medium temperature range of about 600 to 1000 K. We analyzed thermoelectricity and thermal conductivity of ferromagnetic half-metallic half-Heusler MnCoSb[8]. We evaluated the ZT for the Seebeck and anomalous Nernst effect. We discussed carrier and temperature dependence of ZT.

4. Surface Structures and Atomic Radii

To design new functional materials, surface alloying is an effective way to obtain desired materials. Surface alloys are synthesized by inserting atoms into the surface. This topic has attracted a lot of research attention lately because of some of its applications, such as spintronics[11], where there is a giant spin splitting in Bi/Ag(111) surface alloys [12, 13]. Many types of surface alloys have been studied: for example, Ge/Ag(111), Pb/Ag(111), Bi/Ag(111), and Sn/Ag(111). One structure that has been observed in experiments with surfaces is $\sqrt{3} \times \sqrt{3}$ R 30°. Structural studies for surfaces alloys can provide important information for forming metalsemiconductors interface and metal interfaces. The metal-semiconductor interface is very important to industry, for example, the Si/Ag interface is a promising candidate for solar cells. We systematically explored the structural stability of M/Ag(111) surface alloys by first-principles calculation using the OpenMX package[4], where M is group III (B, Al, Ga, In and Tl), IV (C, Si, Ge, Sn and Pb) and V

atom (N, P, As, Sb and Bi). We focused on the corrugation parameter d which is determined by the height of the M atom from the Ag atom in the plane of the top-most atom. We introduced concept of atomic radii to understand the tendencies of corrugation in M/Ag(111). The formation energy for each M atom is also calculated to determine the stability of the surface alloys. We discussed the dependence of M atoms on corrugation parameters.

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Reduction of Rare Metals in Formic Acid Decomposition Catalysts and Oxygen Storage Materials

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We investigated the catalyst adsorption and diffusion properties on non-metal element doped graphene with the aid of the firstprinciples calculation based on the density functional theory (DFT). We also investigated the corresponding catalytic activity. Besides, we investigated the oxygen absorption properties of substituted brownmillerite oxides.

At first, we investigated adsorption and diffusion properties of Cu clusters on nonmetal element doped graphene. We also considered Cu oxide clusters and Cu atoms embedded in the graphene basal plane. We performed the total energy and electronic structure calculations using The Vienna Ab initio simulation package (VASP). We installed a parallelized VASP with Intel® MPI Library and Intel® Math Kernel Library. We found that the adsorption energies and diffusion activation barriers of Cu clusters increase by non-metal element doping into graphene lattice. We note that Cu oxide clusters also show the same trend, and the embedded Cu atoms in graphene have quite high stability. We also investigated the catalytic activity using a theoretical volcano plot reported in the previous study.[1] From the adsorption energy of intermediates, we estimated the reaction activities. We found that the embedded Cu atoms in graphene show higher activity than Cu clusters on graphene.

We also investigated the oxygen absorption properties of partially substituted Ca₂AlMnO₅. We revealed that Mn-site substitution is favorable for the oxygen absorption-desorption process than Al-site substitution.

We also studied the isotope effect on the alkene hydrogenation process on Rh-based Intermetallic catalyst [2] and the structure and magnetism of Ca₂RuO₄ nanofilm.[3]

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Material exploration by advanced first-principles simulation

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The density functional theory (DFT)-based first-principles electronic structure calculation method has played an important role as a powerful research tool in material properties and as a predictor of new materials and structures. We have been developing fundamental simulation methods, such as the accurate calculation of the lattice thermal conductivity using DFT calculations and the prediction of the superconducting transition temperature using superconducting density functional theory (SCDFT), in collaboration with experimentalists.

In this fiscal year, we focused on determining the crystal structure of unknown materials, and predicting the physical properties of these new materials in collaboration with the experimental groups of the Grant-in-Aid for Scientific Research on Innovative Areas "Hydrogenomics: Creation of Innovative Materials, Devices, and Reactive Processes Higher-Order using Hydrogen Functions" (FY 2018-2022) and the Tokodai Institute for Element Strategy. In particular, by developing data-assimilated structure simulation methods based on incomplete experimental data (e.g., incomplete

X-ray diffraction data from high-pressure experiments), we aimed to establish simulation methods that strongly support experimental research on materials under extreme conditions, new materials with only poor quality crystals, and materials containing hydrogen that are difficult to observe experimentally.

In this method, instead of finding the global minimum of the multi-dimensional potential energy surface $E(\mathbf{R})$ as a function of the atomic positions \mathbf{R} , we define the effective potential $F(\mathbf{R})$ by the sum of $E(\mathbf{R})$ and a so-called penalty function $D[I_{obs}, I_{calc}(\mathbf{R})]$, which increases when the simulated diffraction intensity $I_{calc}(\mathbf{R})$ deviates from the experimental one I_{obs} :

$$F(\mathbf{R}) = E(\mathbf{R}) + \alpha ND[I_{\text{obs}}, I_{\text{calc}}(\mathbf{R})].$$

Here, *N* is the number of atoms in the simulation cell and α is a control parameter. Note that, in case of the powder diffraction. I_{obs} and $I_{calc}(\mathbf{R})$ are functions of diffraction angle.

Previously, as a first trial, we adopted "crystallinity" for the penalty function, in which we used diffraction angles but not the diffraction intensity [1]. The method is useful when the relative intensity of diffraction peaks is not reliable. It is, however, not necessarily robust when the crystal symmetry is extremely low, or the noise in the experimental data is very large.

Therefore, in FY 2019, we introduced the correlation between $I_{calc}(\mathbf{R})$ and I_{obs} for the penalty function. With this penalty function, we can treat all the diffraction data, including even the noise, on the same footing and utilize as much information as possible. We found the new penalty function improves the predictability of crystal structures.

We also developed a method to search for structures by treating the potential energy $E(\mathbf{R})$ and the penalty function $D[I_{obs}, I_{calc}(\mathbf{R})]$ independently of each other, using their gradients to avoid local stable solutions [2].

Using these methods, it is possible to search for complex structures containing more than 100 atoms in the simulation cell. However, the search becomes difficult when a specific element in a material is disordered, *i.e.*, a specific element partially occupies multiple sites or arrangements in a unit cell, or two components occupy the same site with a certain probability. Therefore, we also investigated the efficient sampling of the average diffraction pattern of the system (Fig. 1). We are currently working on a test calculation combining this method with the neural network potential.



Fig. 1 An average structure of the hightemperature phase of $LiCB_9H_{10}$ determined by the data assimilation method.

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First-principles study for widening the potential of spinpolarized positron experiments

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polarized Spin positron annihilation technique detected some spin polarized vacancies in semiconductors. We study spinpolarized cation vacancies in wurtzite structure semiconductors (BeO, ZnO, ZnS, CdS, BN, AlN, GaN and GaP) by using first-principles calculations based on the density functional theory. We find that C3v geometries are the most stable and are spin-polarized. Two majority spin electrons occupying the defect E level lead to the magnetic moment of $\mathbf{2}$ μ B in the case of II-VI semiconductors. On the contrary, in the case of III-V semiconductors, three majority spin electrons occupying the defect E and A1 levels induce the magnetic moment of 3 μв.

The spin polarization energies are large in the semiconductors consisting of firstrow anions, i.e., oxides and nitrides. The stabilities in the cases of the oxides and nitrides are due to the fact that the atomic radii of the first raw atoms are small and thus the spin densities are substantially localized at the four nearest anions in. the cation vacancies.

Finally, we study the symmetry lowering effect from C3v to Cs which reduces the magnetic moments; we study the possibilities of both pairing and departing distortions. The magnetic moment becomes 0 in the case of II-VI semiconductors and the magnetic moments become 1 μ B in the case of III-V semiconductors. We find that these low spin states have higher energies than the C3v high spin states due to the fact that the symmetry lowering effect do not significantly stabilize the system.

Unification of massively parallel quantum material simulation and data-driven science

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The present project was carried out for the joint research between quantum material simulation and data driven science. Related mathematical studies and software development were also carried out. The main collaborators are K. Tanaka (Tottori U, D. student), H. Imachi (Tottori U, now in Preferred Networks), K. Yoshimi (ISSP), I. Mochizuki, T. Hyodo (KEK-IMSS), T. Fujita (IMS), T. Fukaya (Hokkaido U), Y. Yamamoto (UEC), H. Matsui (Yamagata U) and T. Ogita (TWCU).

The main achievements are explained hereafter. (i) The data analysis software was developed for total-reflection high-energy positron diffraction (TRHEPD), a novel experimental technique for surface structure determination [1,2]. Experiments using TRHEPD are being conducted intensively at the Slow Positron Facility, Institute of Materials Structure Science, High Energy Accelerator Research Organization, revealing surface structure of interest. Figure 1 demonstrates the structure determination of the Ge(001)-c(4x2) surface [2]. At April of 2020, software development activity was the promoted to Project for Advancement of Software Usability in Materials Science in ISSP

https://www.pasums.issp.u-tokyo.ac.jp (). Since the analysis method has a general mathematical foundation, it is also applicable to other experiments, such as X-ray or electron diffraction experiments. (ii) Large-scale electronic structure calculations were carried out for a 10-nm-scale pentacene thin film as a foundation of flexible transistor [3]. Semilocalized wavefunctions that expand over several tens of molecules were obtained, which is consistent to electron spin resonance experiment. The study was carried out by our original code ELSES (http://www.elses.jp/), an order-N electronic state calculation code with a *ab initio* based tight-binding method. In addition, several fundamental methodologies were developed for large-scale calculation of organic flexible device materials [4,5]. (iii) Several fundamental numerical algorithms were investigated [6-8]. (iv) Two books were published for reviews of our recent research activities in large-scale electronic structure calculations with supercomputers [9,10].

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Fig.1 (a) Schematic figure of totalreflection high-energy positron diffraction (TRHEPD) experiment.
(b) The data analysis of experimental TRHEPD data for Ge(001)-c(4x2) surface [2].

Reduction of Rare Metals in Fuel Cell Catalysts and Hydrogen Permeable Membrane

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We investigated the catalyst adsorption and diffusion properties on non-metal element doped graphene and hydrogen dissolution and diffusion properties in the interfaces of ceramic materials, with the aid of the firstprinciples calculation based on the density functional theory (DFT).

At first, we investigated adsorption and diffusion properties of Pt clusters on nonmetal element doped graphene. This year, we also considered Pt atoms embedded in the graphene basal plane. We performed the total energy and electronic structure calculations using The Vienna Ab initio simulation package (VASP). We installed a parallelized VASP with Intel® MPI Library and Intel® Math Kernel Library. We found that the adsorption energies and diffusion activation barriers of Pt clusters on graphene increase by substitutional non-metal element doping. This is because of the strong covalent bonds between the Pt atom and substitutional dopants. Therefore, we concluded that these dopants in graphene can prevent the detachment and surface diffusion of Pt clusters. We also investigated the catalytic

activity of Pt clusters on non-metal element doped graphene based on the energy diagram.[1] We revealed that the Pt clusters show less support effect than Pt single atoms.

We also investigated the hydrogen dissolution and diffusion properties in the interfaces of TiN containing O impurities. We found that H atoms do not prefer the O sites.

We also studied the tunneling effect on the alkene hydrogenation process on Rh-based Intermetallic catalyst using quantum dynamics simulation of atomic nuclei [2] and thickness dependence of the structure and magnetism of Ca₂RuO₄ nanofilm.[3]

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Ab-initio analysis of phonon and electron-phonon interaction

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Heat generation in semiconducting materials has become a critical problem in modern nanoscale electronics. As the size of electric devices decreases, the power density and device temperature increase, which is one of the major factors contributing to the degradation of device performance and reliability.

The main carrier of heat in semiconductors is the phonon, which is a quantum of lattice vibration. Current theoretical frameworks require accurate prediction of the interatomic force in the solid. Density functional theory (DFT) calculation is one of the most wellestablished techniques for accurate force prediction, including the effect of changes in the electronic state with atomic displacement. However, the high computational cost limits the application of DFT calculation in thermal conductivity simulations.

We apply the high-dimensional neural network potential (HDNNP). We generated the random but reasonable structures were first generated from the trajectories of classical molecular dynamics simulations, and then the energy and forces in each structure were evaluated by DFT. These DFT calculation results are used as dataset to train HDNNP. We found that the training procedure based on force makes the root mean square error between the forces predicted by HDNNP and DFT less than 40 meV/Å. As typical examples, we present the results of Si and GaN bulk crystals. The deviation from the thermal conductivity calculated using DFT is within 1% at 200 to 500 K for Si and within 5.4% at 200 to 1000 K for GaN.



Fig. 1 Comparison of thermal conductivity obtained from DFT calculation and HDNNP for bulk Si (a) and GaN (b).

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Electrochemical Reaction Analysis Using Density Functional Calculation + Implicit Solvation Model

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We have studied charge transfer reaction at electrode/electrolyte solution interfaces in Liion batteries (LIB) using density functional theory (DFT) calculation combined with implicit solvation model. This simulation is called ESM-RISM,1 i.e., the effective screening medium (ESM)₂ + the reference interaction site model (RISM)₃, and implemented in Quantum Espresso package.4

This year, we focused on Li-ion transfer reaction (R) at the interface of graphite electrode/solid electrolyte interphase (SEI)/ solution (1 M LiPF₆ EC) as follows:

 $\operatorname{LinC6mH}_{l} + h\operatorname{Li2CO3} \rightarrow \operatorname{Lin-1C6mH}_{l} + h\operatorname{Li2CO3} + \operatorname{Li+(1 \ M \ LiPF6 \ EC)} (R).$

ESM-RISM calculations were performed on the configuration of a vacuum/slab/soltion system as shown in Fig. 1 (a), where the DFT slab domain represents Li-inserted graphite $(Li_nC_{6m}H_l)/SEI$ (inorganic lithium carbonic acid, hLi_2CO_3), and the RISM solvent and ions, (EC, Li+, and PF₆-). Since the electrolyte concentration of typically 1.0 M gives a small Debye screening length of several angstroms, the RISM region (> 40 Å) used in this calculation was sufficiently long.

Figure 1 (b) shows the grand potential Ω of pristine, Li_nC_{6m}H_I/hLi₂CO₃, and V_{Li} + Li+, Li_{n-1}C_{6m}H_I/hLi₂CO₃ + Li+(1 M LiPF6 EC), as a function of the chemical potential of an electron μ_e . In the ESM-RISM calculations, μ_e is measured from the potential at inner solution region Φ s. It is possible to compare μ_e at different electrodes contacting the same solution directly.5 The difference between two equilibrium potentials on different electrodes provides the electromotive force, E_{emf} , between the two electrodes as:

$$E_{\rm emf} = -(\mu_{\rm eq} - \mu_{\rm Li/Li+})/e$$
 (1),

where μ_{eq} represent the equilibrium potential of reaction (*R*) and *e* is the elementary charge. Once an equilibrium potential μ_{Li/Li^+} of Li transfer reaction at Li metal electrode is determined in the ESM-RISM calculation, the electromotive force (or electrode potential relative to the Li/Li+ reference) can be immediately derived. Because it was obtained $\mu_{Li/Li^+} = -3.06 \text{ eV vs } \Phi \text{s}$ in a previous study,6 the result of $\mu_{eq} = -3.17 \text{ eV vs } \Phi \text{s}$ gave $E_{emf} =$ 0.11 V vs Li/Li+, which is in good agreement with experiment (0.1 – 0.2 V vs Li/Li+).



Fig. 1: (a) ESM-RISM configurations of the vacuum/slab/solvent system: the simulation cells of Li_nC_{6m}H_l/hLi₂CO₃|1M LiPF₆ EC interfaces. (b) Profiles of Ω as a function of μ e. The blue and orange lines show Ω of Li_nC_{6m}H_l/hLi₂CO₃ and Li_{n-1}C_{6m}H_l/hLi₂CO₃ + Li+(1 M LiPF₆ EC), respectively.

Additionally, it was confirmed that the equilibrium potential of reaction (R) cannot depend on such as the thickness and component of SEI. In the next physical year, the activation energy of reaction (R) will be revealed under operated LIB working conditions.

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Van der Waals density functional study of molecules adsorbed on metal surfaces

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Accurate description of the moleculesurface interaction is prerequisite for precise understanding of chemical processes at surfaces and interfaces in diverse systems including electrochemical energy conversion devices such as fuel cell, photoelectrochemical cell, and rechargeable battery, as well as heterogeneous catalyst for emission control, name only a few. For this purpose, the van der Waals density functional (vdW-DF) [1] and its variants have been used to study a variety of systems and proven accurate in describing molecule/surface interfaces, as well as bulk systems.

In this project, we have studied quasi one dimensional chain composed exclusively of pentagonal water on Cu(110). In particular, we have studied the small water clusters on Cu(110) to investigate the origin of the pentagonal water chain.

All the calculations were performed using STATE, our in-house plane-wave pseudopotential code. We used an efficient implementation [2,3] of the self-consistent vdW-DF. The rev-vdW-DF2 functional was used [5].

Previously we constructed and optimized

water clusters from monomer to hexamer, and found that the pentagonal water cluster is more stable than the hexagonal one on Cu(110). We further constructed larger water clusters such as octamers composed of pentamers, nonamers composed of pentagon and hexagon, those with two pentagons plus water monomer, and dimer composed of pentamers. We found that the clusters composed of pentagons are consistently more stable and that the calculated water clusters can explain the high-resolution noncontact atomic force microscopy images [6]. Furthermore, we found that the 2D ice rule applies to explaining and predicting the structure of water clusters on Cu(110).

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Energy Transport in Hybrid Organic-Inorganic Thermoelectric Materials

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Thermoelectric materials can directly convert waste heat energy to useful electricity. During the last decade, the organic polymers have shown unique features such as low density, low thermal conductivity, easy synthesis and versatile process ability. Using organic polymers in thermoelectric materials appears to have great potential for producing relatively low cost and high performance thermoelectric devices. However, little work on modeling and simulation is reported at present.

The first main part of last year work is thermoelectric about the property investigation of metastable phases of silicon. In this work, the phonon and electron transport properties of metastable Si-III and Si-XII are investigated by density functional theory, as shown in Fig 1 and 2. The metastable Si-III and Si-XII show one magnitude lower thermal conductivity than the stable Si-I phase. The effect of different three-phonon scattering processes on the thermal conductivity of different phases were evaluated by removing specific scattering processes from the Brillouin zone. Further electron transport property calculation suggests that the metastable Si-III and Si-XII phases have higher thermoelectric figure-of-merit than the Si-I phase in

which the low lattice thermal conductivity and the high electrical conductivity at low chemical potential region contributes the most. The results suggest an effective way to improve the thermoelectric performance of Si-based materials.







Figure 2: Comparison of electron transport property in Si-I, Si-III and Si-XII.

The second main part of last year work is about the design of magnetic tunnel (MTJs) junctions using disordered MgAl₂O₄. Through Bayesian optimization and the least absolute shrinkage and selection operator technique combined with first-principles calculations, we investigated the tunnel magnetoresistance (TMR) effect of Fe/disordered-MgAl₂O₄(MAO)/Fe(001) magnetic tunnel junctions to determine structures of disordered-MAO that give large TMR ratios. The optimal structure with the largest TMR ratio was obtained by Bayesian optimization with 1728 structural where candidates, the convergence was reached within 300 structure calculations. Characterization of the obtained structures suggested that the in-plane distance between two Al atoms plays an important role in determining the TMR ratio. Since the Al-Al distance of disordered MAO significantly affects the imaginary part of complex band structures, the majority-spin conductance of the $\Delta 1$ state in Fe/disordered-MAO/Fe MTJs increases with increasing in-plane Al-Al distance, leading to larger TMR ratios. Furthermore, we found that the TMR ratio tended to be large when the ratio of the number of Al, Mg, and vacancies in the [001] plane was 2:1:1, indicating that the control of Al atomic positions is essential to enhancing the TMR ratio in MTJs with disordered MAO. The present work reveals the effectiveness and advantage of material informatics combined with firstprinciples transport calculations in designing high-performance spintronic devices based on MTJs.



Figure 3: Schematics of designing magnetic tunnel junction for high tunnel magneto-resistance ratio by combining Bayesian optimization and first-principles calculation.

In summary: (1) We have shown that metastable Si-III and Si-XII phases have higher thermoelectric figure-of-merit than the Si-I phase. (2) We have successfully designed the optimal disordered Fe/ MgAl₂O₄/Fe (001) structure with the highest tunnel magnetoresistance ratio optimal by combining the first-principles transport calculations and Bayesian optimization.

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Quantum Chemical Analysis for High-Performance Polymer Electret

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Electret is dielectric material with quasipermanent charges. Vibration Electret Energy harvesting (VEEH) is a clean way to convert environmental energy into electricity by electrostatic induction more efficiently than electromagnetic or piezoelectric counterparts [1]. VEEH can be applied to low power electronics such as wireless sensors, implantable medical equipment and wearable device. Since the power output of the VEEH is proportional to the square of surface potential of the electret, it is necessary to discover electret material with high surface charge density. Furthermore, if we could find electret suitable for both negative and positive charging, the power output of VEEH will boom by 4 times theoretically.

CYTOP (AGC Co. Ltd.) is a fluorinated amorphous polymer, with its chemical structures shown in Figure 1. There are three kinds of commercialized CYTOP, S, A and M. CTX-A has carboxyl end groups and CTX-M has alkoxysilane/amide end groups. According to quantum chemical analysis of CYTOP series with different end groups, the amino bond formed after reaction can act as a strong charge trapping site [2]. Therefore, we investigate charge stability of candidates with free amine functional group which can react with -COOH end group of CTX-A. Electron affinity and ionization potential obtained from quantum chemical calculation are used to evaluate the electron trap energy and hole trap energy of possible candidates after dehydration condensation respectively.

Electron affinity is calculated by comparing molecular energy at neutral and negatively-charged state while ionization potential is computed by comparing molecular energy at neutral and positivelycharged state. The calculated ionization potential of CYTOP based electret is as follows: 13.12 eV (CTX-S), 12.03 eV (CTX- A), 9.81 eV (CTX-M) and 7.81 eV (CTX-A/TAEA). Figure 2 visualizes the



Fig. 1. Chemical structure of CYTOP series.



Fig. 2. Visualization of hole trapped orbitals for positive state of CTX-A/TAEA.



Fig. 3. Normalized TSD spectra of CYTOP electrets charged to +2 kV.

hole trapped orbitals of positively charged CTX-A/TAEA monomer. It is shown that the hole is located near the amide bond, which is formed by the reaction between the carboxy end group and TAEA.

Thermally stimulated discharge (TSD) measurement is also done for comparison between calculation and experiment. Figure 3 shows the TSD spectra of CYTOP polymers for positive charging. It is found that CTX-A/TAEA has the highest charge thermal stability with smallest computed ionization potential value. In addition, the TSD spectra for positive charging exhibit multiple peaks, indicating the difference in the charge trapping mechanisms between negative and positive charges [3], which will be analyzed in the future.

This work was partially supported by JST CREST Grant Number JPMJCR15Q3 and JPMJCR19Q1, Japan. The calculation is performed with SGI ICE XA ISSP system B and every calculation is held with 1 node (24 CPUs). The energy of the molecule is computed by DFT to CAM-B3LYP/6-31+G(d,p) level by using quantum chemical simulation software GAUSSIAN [4]. Molecular dynamic simulation package GROMACS [5] and solid-state analysis package VOTCA-CTP are also used [6] for more accurate estimation. In case of CYTOP hexamers, the calculation cost is approximately 150 CPU hours for quantum chemical calculation, 100 CPU hours for MD simulation and 5 CPU hours for multipole analysis and solid-state analysis.

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Theoretical modeling of carrier localization/delocalization and related phase transitions

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1 Introduction

We investigate trends in carrier localization in defective semiconductor/insulator systems focusing on phase transitions. We have previously illustrated the mechanistic origin of the Mott transition and related excitonic insulator phases [1], as well as strain induced piezomagnetic transitions in magnetic semiconductors [2]. This year, we have clarified carrier-induced magnetic transitions in transition-metal doped Ga_2O_3 systems [3, 4], as well as charge trapping in resistive memory (ReRAM) devices [5]. Also, an introductory review of first principles methods for defects in semiconductors/insulators was published as a book chapter [6].

2 Ga_2O_3 systems

We carry out density-functional calcualtions using the VASP code with in-house developed corrections for band-gap [7] and selfinteraction [2]. Band-gap correction of Ga₂O₃ is achieved applying non-local external potential parameters as follows. $V_{O,s}^{NLEP}$ =-6.4 eV, $V_{O,p}^{NLEP}$ =-2.0 eV for oxygen [7], and for Ga, we use $V_{Ga,s}^{NLEP}$ =10.0 eV, $V_{Ga,p}^{NLEP}$ =2.5 eV, and $U_{Ga,d}$ =9.0 eV to achieve best fit of several physical parameters (see Table 1). For Cr 3*d*, we set *U*=2.6 and *J*=1.0 eV. [7] We further cross-validate these parameters against selfinteraction corrected VP-SIC in the KKR-CPA framework (see [3] for details).

Table 1: Physical properties of β -Ga₂O₃. E_g is band gap energy (eV) and m_e^* is effective electron mass.[3]

	pure GGA	GGA+NLEP	Exp.
$a(\text{\AA})$	12.40	11.90	12.214
b/a	0.250	0.251	0.249
c/a	0.475	0.471	0.475
$V(\text{\AA}^3)$	219.43	197.26	208.85
$\Delta V(\%)$	+5.1	-5.5	
$\beta(\deg)$	103.8	104.1	103.82
E_g	2.0	4.7	4.9
m_e^*/m_e	0.19	0.37	0.28

Carrier-mediated ferromagnetism in Crdoped β -Ga₂O₃. [3] First of all, we find that Cr prefers the octahedral lattice site in β -Ga₂O₃ by $\sim 1 \text{ eV}$ against the tetrahedral site. We then show that Cr in the octahedral site has a negative charge transition close to conduction band minimum, so the system may become charged. Magnetic interaction among Cr impurities is investigated as a function of Cr–Cr distance up to ~ 8.5 Å. For nonconductive systems, we find a weak antiferromagnetic coupling for nearest neighbor Cr–Cr pairs, and zero interaction for all other pairs investigated. We then include carrier-electrons, which cause negative charging of Cr impurities. We further find that such carrier-doping switches on a strong ferromagnetic interaction, which persists up to ~ 6 ÅCr–Cr separation.

Optical properties ϵ and κ phases of Ga_2O_3 doped with cobalt. [4] In collaboration with experimental work, we investigate the modulation of optical absorption edge in ϵ and κ phases of Ga_2O_3 by Co doping. Co impurity levels, as well as those of some typical native impurities, are calculated from first principles. We then calculate the optical absorbance for several Co doped systems at several defect concentrations. This is used to re-interpret experimental observations, which previously asserted band-gap modulation based on changes in optical gap upon Co doping. However, our calculation shows that the optical gap changes instead are due to Co impurity levels. We further present a new band diagram to clarify changes in work function due to Co doping in these systems.

3 Charge trapping in ReRAM systems

We describe resistive memory ReRAM devices by a metal/insulator/metal sandwich structure, and investigate charge trapping by numerically solving Poisson's equation. We develop a self-consistent Poisson solver, where charge stored in device is solved selfconsistently together with potential over device under different bias voltages. We discover new band-bending solutions characterized by different amount of charged stored in the system, and reversible switching between these differently charged states, illustrated in Figure 1. This electrostatic switching mechanism provides a novel interpretation for ReRAM operation, and resolves the mystery of extremely fast sub-nanosecond switching.

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Figure 1: Band bending solutions of ReRAM device, and switching by external bias.

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Ab initio study on the metallization and superconductivity in metallic superhydrides

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In this project, we studied the mechanism of the metallic and superconducting properties of the superhydrides-the compounds containing anomalously large formula ratio of hydrogenrecently synthesized under megabar pressures. The discovery of the 200-kelvin superconductivity in the compressed H_2S (Ref. [1]) has triggered extensive study on the pressure induced superconductivity of hydrogen compounds. Later studies revealed that the novel phase containing excess hydrogen atoms, H_3S , emerges under extreme pressures, which is responsible for the experimentally observed high- $T_{\rm c}$ superconductivity. This has motivated the exploration of pressure induced hydrogenexcess compounds.

First, we numerically examined the superconducting properties of some crystalline lanthanum and yttrium superhydrides, LaH_x and YH_x , for possible explanation of the experimentally observed superconducting transition temperature (T_c) (260 K and 240 K, respectively) in these systems. We calculated T_c for theoretically predicted crystal structures of LaH₁₀ and LaH₁₆ from first principles. Specifically, we solved the gap equation of the density functional theory for superconductors (SCDFT) (Ref. [2, 3, 4])

$$\Delta_{n\mathbf{k}} = -\mathcal{Z}_{n\mathbf{k}}\Delta_{n\mathbf{k}} - \frac{1}{2}\sum_{n\mathbf{k}}\mathcal{K}_{n\mathbf{k}n'\mathbf{k}'}\frac{\tanh\frac{\beta E_{n'\mathbf{k}'}}{2}}{E_{n'\mathbf{k}'}}\Delta_{n'\mathbf{k}'}$$

Here, the phonon-mediated Cooper pairing effect is included within the Eliashberg theory with the Migdal approximation. Also, the electron-electron Coulomb repulsion that suppresses the pairing is also incorporated. Δ is the order parameter and $n\mathbf{k}$ labels the Kohn-Sham band index and crystal wavenumber, respectively. $E_{n\mathbf{k}} = \sqrt{\xi_{n\mathbf{k}}^2 + \Delta_{n\mathbf{k}}^2}$ and β is the inverse temperature. The non-diagonal part of the kernel of Eq. (1) \mathcal{K} is composed of the phononic and electronic contributions: $\mathcal{K} = \mathcal{K}^{\text{ph}} + \mathcal{K}^{\text{el}}$. On the other hand, the diagonal part \mathcal{Z} includes only the phononic one: $\mathcal{Z} = \mathcal{Z}^{\text{ph}}$. To evaluate the phononic parts we need to calculate the Eliashberg function $\alpha^2 F(\omega)$, which is roughly the phonon density of states weighted by the coupling strength to the electrons. The electronic part is calculated as the two-particle matrix element of the screened Coulomb interaction, where the one-particle states and dielectric function are calculated by the first-principles Kohn-Sham equation. All the components were calculated with the plane-wave basis code package QUAN-TUM ESPRESSO (Ref. [5]). The phononic properties of the yttrium compound was supplemented with the anharmonic correction using the stochastic self consistent harmonic approximation [6].

We show in Table I the values of T_c calculated with the SCDFT gap equation [Eq.(1)], as well as characteristic parameters of $\alpha^2 F(\omega)$

(1)
$$\lambda = 2 \int d\omega \frac{\alpha^2 F(\omega)}{\omega}, \qquad (2)$$

$$\omega_{\rm ln} = \exp\left[\frac{2}{\lambda} \int d\omega \frac{\alpha^2 F(\omega)}{\omega} \log\omega\right].$$
 (3)



Figure 1: (a) Crystal structure of the high- T_c phase of cubic H₃S and its band structure and DOS. The thin and bold lines represent the first-principle and Wannier band structures, respectively. (b) The simple cubic Brillouin zone and positions of the loop-like continuous saddle points in the band structures. (c) The minimal Wannier model that reproduces the saddle loop around the M point. See Ref. [12] for more details.

Table 1: Coupling constant λ (Eq. (2)), typical frequency $\omega_{\rm ln}$ (Eq. (3)), and the superconducting transition temperature $T_{\rm c}$ calculated with the SCDFT gap equation Eq. (1).

	LaH_x [9]		YH_x
	LaH_{10}	LaH_{16}	YH_6
Pressure (GPa)	200	200	165
λ	3.75	1.82	1.71
$\omega_{ m ln}$	905	1366	1332
$T_{\rm c}~({\rm K})$	271	156	156

Experimentally observed T_c for the lanthanum systems strongly depends on the trials [7, 8]. The synthesis with excess hydrogen yielded T_c varying from 250 K to 210 K. Our calculation indicates that the high- T_c phase corresponds to LaH₁₀ (left column), whereas the low- T_c phase could be a mixture of LaH₁₀ and LaH₁₆ (middle column). We have published this result in Ref. [9]. For the yttrium hydride, on the other hand, our calculated T_c (right column) was substantially lower than the experimental value (~ 240 K). At this point we have not reached to a plausible understanding of the origin of the discrepancy [10].

We also addressed the metallic electronic

state in the sulfur superhydride H₃S. According to preceding studies, it hosts a sharp peak at the Fermi level in the electronic density of states (DOS) N(E) (Fig. 1 (a)), which has a role of boosting the T_c via the relation $\lambda \propto$ $N(E_{\rm F})$ with $E_{\rm F}$ being the Fermi level. Its origin has, however, yet been clarified. To elucidate the mechanism of its formation, we first performed a close analysis of the band structure and found that the DOS peak structure mainly originates from the loop-like continuous saddle points around the M point in the primitive cubic Brillouin zone (Fig. 1 (b)). Next, we constructed the Wannier model using QUAN-TUM ESPRESSO and WANNIER90 (Ref. [11] program packages. Our model consists of sulfurs, p and hydrogen-s like orbitals and almost perfectly reproduces the first-principles band structure especially around the Fermi level (Fig. 1 (a)). We then calculated the effective band structures with this Wannier model with omitting the interorbital hopping parameters. Finally, we found that a simple model reproduces the key feature in the band structure; the saddle-point loops around the M point. In this model (Fig. 1 (c)), the simple cubic ScF_3 sites and the nearest-neighbor and selected farther neighbor hopping parameters have been extracted from the original Wannier model. The nearest-neighbor hoppings for the *s*-like and *p*-like orbitals on the simple cubic ScF₃ lattice geometry yields a saddle point at the M point, and in addition, the selected farther neighbor hopping "pushes down" the state at the M point to form the continuous loop of the saddle point. This understanding on the origin of the DOS peak in the celebrated high- T_c superconductor H₃S has been published [12].

Computational detail. The generalized gradient approximation for the exchangecorrelation potential was employed [13] for the calculations of LaH_x , YH_x and H_3S . MPI parallelized calculations were performed with respect to k points (-npool option) as implemented in pw.x code. The screened electronelectron Coulomb matrix elements [4] were calculated with an in-house code with the OPENMP parallelization. The calculations were mainly done in System B.

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First-principles study on physics of gap-state control at metal/semiconductor interfaces

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Due to the break of atomic bonds and the lack of translational symmetry, gap states appear in semiconductor layers around metal/semiconductor interfaces, which have the energy position in the band gap and are localized around the interface. These states induce the electron transfer between metal and semiconductor layers and determine a variety of physical phenomena at the interface, such as Schottky barrier (SB), defect density, and metal-atom ionization. However, it is still unclear how to control the gap states. In this works, we studied the SB and tunneling current at various interfaces and clarify the origins of gap-state generation/annihilation and deformation using the first- principles calculations.

We first consider metal/Ge interfaces, where Fermi energies of most of metals are located around the valence-band top of Ge irrespective of the kinds of metals. This is called the Fermi-level (FL) pinning and interrupts desirable low-resistive metal/n-Ge contacts. Although the breakdown of FL pinning was recently observed at TiN/Ge(001) interfaces, its origin has not been clarified. To simulate the interfaces, we adopt (1×1) -- (3×3) TiN/Ge(01) repeated-slab models with various interface structures and calculate their SBs using local potential profiles.

Figure 1 shows calculated SBs for hole carriers ate various interfaces. The SBs at Ti-rich interfaces like abrupt (a-2) are around 0.0eV corresponding to the FL pinning, while the SBs at N-rich interfaces such as (b-2) and (c) have large values above 0.3eV, which is in good agreement with experiments. The origin of such SB variation is understood by observing the projected densities of states (PDOS) of interface atoms, which are shown in Fig.2.



Fig.1. Left: calculated Schottky barriers for hole carriers at various TiN/Ge interfaces. Right: schematic pictures of interface structures. (a-2): abrupt Ti-rich interface, (b-2) and (c): N-rich interfaces with TiN_2 and Ge_3N_4 interface layers.

For (a-2) interface, the continuous PDOS, thus the gap states, appear around 0.0eV for interface Ge atoms due to the orbital hybridization between Ti and Ge, which induces electron transfer from TiN to Ge and realizes the FL pinning. On the other hand, we can see the suppression of gap states in the PDOS of interface Ge for (b-2) interface, which is caused by the production of interface N-Ge bonds. In this way, the interface covalent bonds eliminate the gap states in interface Ge layers.

Next, we consider how the interface bonds affect the SBs. We artificially produce metal/X/Ge(001) interfaces with various segregation atoms, X, that terminate interface Ge, and calculate the SBs, the results being shown in Fig.3 for Al/X/Ge cases. We found the chemical trend that the segregation of IIand III-family atoms lowers the SBs, while that of V- and VI-family atoms raises the SBs. By analyzing electronic structures in details, it was shown that such trend reflects the valency of X



Fig.2. Calculated projected densities of states of interface atoms around TiN/Ge interfaces with (a-2) and (b-2) structures shown in Fig.1. Ge(1) and Ge(2) correspond to the first and second layer germanium atoms, respectively.



Fig.3. Calculated Schottky barriers for hole carriers at Al/X/Ge interfaces with various segregation atoms, X. Ec and Ev denote the conduction-band-bottom and valence-band-top positions of bulk Ge, respectively.

atoms; when X-Ge bonds are produced at the interface, the electron transfer occurs from X to Ge for X atoms with less than 4 valence electrons, while the additional transfer occurs from X to Al for X atoms having more than 4 electrons. In this way, not only the termination of interface Ge bonds but also the kinds of termination atom is important to deform the gap state and depin the FL.

Finally, we study how the gap states change in electric field. We consider the tunneling current at



Fig.4. (a): calculated tunneling probability of electrons at Si-p/n junction as a function of electric field, for the cases with (red line) and without (blue) dopants. (b) and (c): energy distribution of tunneling electrons and resonance state at doped p/n junction.

Si-p/n junction. Figure 4(a) shows calculated current as a function of applied electric field. When the dopant is embedded in p/n junction (red line), the current is markedly enhanced, which is caused by the tunneling through the dopant state as seen in the energy spectra in Fig. 2(b). Figure 2(c) shows a wavefunction of such dopant state. This state is a resonance state between isolated dopant state and gap state produced by the penetration of conduction-band state of right-handed bulk Si layers into the band gap. By changing not only the spacial and energy positions of dopant state but also the electric field, we can control such resonance. In this way, the gap-state characteristics are controlled by the electric field.

All these calculations were performed using the xTAPP, VASP, and pspwf codes. In order to realize the calculations for the present interface systems, because the system is made of a large number of atoms (300-1000 atoms), the advanced computing facility having multi-task and higher-speed CPU (more than 64 cores \times 2.5GHz), larger-size memory (around 128GB), and larger-size strange (more than 1 TB) is indispensable. These conditions are realized only by the ISSP supercomputing systems.

Theoretical analysis of ion conduction mechanism of highly concentrated electrolytes for secondary batteries

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Highly concentrated electrolytes have recently attracted much attention owing to their unique electrochemical properties derived from an unusual coordination structure, where the ligand (solvent/anion) exchange reactions are responsible for the ion transport, while the vehicular-type mechanism is dominant in the diluted electrolyte [1]. Herein, we theoretically investigated the salt concentration dependence of ionic conduction mechanism in AFSA/DME electrolyte (A = Li, Na, K) using quantum molecular dynamics (MD) simulations.

All the calculations were performed using divide-and-conquer density functional tightbinding (DC-DFTB) method [2]. A modified 3OB parameter set based on first-principles calculations was adopted, and a constant temperature condition of 298.15 K was imposed under *NVT* ensemble. The equilibration of 10 ps at 1 fs time interval was followed by the sampling of 200 ps.

With increasing the salt concentration, the ligand exchange reactions become active mainly via FSA anions (Fig. 1). The increased ion radius (decreased Lewis acidity) of cations also activates the ligand exchange reactions by weakening the interaction with the ligands. Therefore, both the higher concentration and increased cation size should promote the ligand exchange-type ion transport.

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Fig. 1 Relationships between frequencies of ligand exchange, A, and salt concentration.

First-principles Theoretical Study of Chemical Reactions in Heterogeneous Catalysts

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In 2019-2020, we carried out theoretical analysis of chemical processes at surfaces and interfaces, formic acid adsorption and decomposition on Cu(111) [1], enhancement of CO₂ hydrogenation by O-C-O bending vibration mode [2], trimer formation of NO Cu(111) [3], and CO oxidation and oxygen reduction reaction at Pt single atom catalyst supported by graphene edges [4]. We also investigated dopant in semiconductors, namely, transition metal doped ZnSnAs₂ [5], and As and B codoping in Si [6]. In this report, we report the enhancement of CO₂ hydrogenation by vibration excitation [2].

Recently, formic acid (HCOOH) has been considered as a potential material for hydrogen storage. Storage of HCOOH is easier and safer compared with other hydrogen storage material because HCOOH is a non flammable liquid at STP. HCOOH can be decomposed on metal surfaces through dehydrogenation process into CO_2 and H_2 , or dehydration process into COand H_2O . Cu catalysts have been reported to selectively decompose HCOOH through dehydrogenation process. The decomposition of HCOOH does not occur on Cu(111) when exposed to the gas phase HCOOH at room temperature. On the Cu(111) surface, HCOOH was reported to form polymeric structures when exposed to the gas phase HCOOH at low temperatures, then the decomposition occurs by heating those polymeric HCOOH.

In the present study, we have investigated

the adsorption and decomposition mechanisms of monomeric HCOOH on Cu(111) by using density functionals that account for the vdW forces and compared with room temperature experimental results.

Our calculations were performed using the STATE (Simulation Tool for Atom TEchnology) code[7]. Here, we compared results obtained using the PBE functional with those using the van der Waals density functionals (vdW-DFs), i.e., optB86b-vdW and rev-vdW-DF2 [8] functionals. We also included the dispersion correction proposed by Grimme with PBE (PBE-D2). The implementation of the self-consistent vdW-DF in the STATE code is described in Ref. [9].

The reaction path for the decomposition (E_{dec}) of the OH-perpendicular configuration on the Cu(111) surface is shown in Fig. 1. The calculated activation energies of decomposition $(E_{dec}$'s) with ZPE correction are 0.37 eV, 0.31 eV, 0.32 eV, and 0.30 eV for PBE, PBE-D2, rev-vdW-DF2, and optB86b-vdW functionals, respectively, indicating that the E_{dec} are almost independent among the considered functionals in this work. PBE-D2 and vdW-DFs produce lower E_{dec} than E_{des} by (0.16–0.27 eV).

Figure 2 shows the calculated desorption and decomposition rates per surface adsorbate. In this analysis, we used the calculated results by rev-vdW-DF2 energy functional. At low temperatures, the decomposition process



Figure 1: (a) Decomposition process of the OH-perpendicular configuration. IS, TS, and FS represent initial state, transition state, and final state, respectively. (b) Energy profile for the OH-perpendicular configuration decomposition on Cu(111).



Figure 2: Calculated reaction rates per surface adsorbate for the desorption and decomposition of OH-perpendicular configuration. Red dashed line with circle and blue solid line with square dots line represent the decomposition and desorption rates obtained by using the 2D lattice gas, respectively.

becomes faster than the desorption process, while at higher temperatures, the desorption process becomes dominant due to large preexponential factor for the desorption process and the transition temperature between the two processes is ~ 187 K. These results are in very good agreement with the experimental situation that there is no HCOOH decomposition on Cu(111) by exposing the surface to the gas phase HCOOH at room temperature.

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Theoretical Design of Gate Dielectrics of Future GaN Power Devices

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We performed the density-functional calculations that clarify atomic and electronic structures of the oxygen vacancy Vo in amorphous (Al₂O₃)_{1-x}(SiO₂)_x mixed oxides, a promising candidate for the gate insulator in future GaN power devices [1]. We constructed microscopic models for the amorphous structure by the melt-quench scheme and then examine all the possible oxygen vacancies and determine the total-energy minimized Vo structures. We found a clear tendency that the Vo formed at the oxygen site surrounded by less Al atoms has lower formation energy. More importantly, we find that Vo surrounded by Si atoms alone induces no deep levels in the energy gap of GaN, whereas Vo surrounded by more Al atoms induces a deep level. This theoretical finding strongly infers that the majority of Vo in amorphous $(Al_2O_3)_{1-x}(SiO_2)_x$ is electrically inactive and not very harmful in device operations. We further explore the possibilities of the structural transformation from the electrically active V₀ to the electrically inactive Vo. We identified reaction pathways for such transformation and obtain the corresponding

energy barriers. The calculated occurrence rate for the transformation is high enough to assure that the thermal annealing at typical temperature and time causes the conversion of the electrically active V_0 to the inactive V_0 , providing a further advantage of $(Al_2O_{3)l}_x(SiO_2)_x$ as the gate insulator over other oxides such as SiO₂ and Al₂O₃.



Fig.1: Density of states of the (Al2O3)0.70(SiO2)0.30 mixed oxide containing a single oxygen vacancy VO obtained by HSE, (a) surrounded by Al atoms and (b) surrounded by Si atoms. The origin of the energy is set at the valence band maximum. (c) Atomic structure of a Vo surrounded by Si atoms. A Si-Si bond is formed after removal of the oxygen atom. Silver, blue, and red spheres represent the Al, Si, and O atoms, respectively.

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Analysis of Thermoelectric Properties of Clathrate Compounds with *Ab Initio* Calculations

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Clathrate compounds promising are candidates for thermoelectric materials in terms of the "electron-crystal phonon-glass" concept. Clathrate compounds are composed of guest atoms encapsulated in cagelike structures. It is expected that electrons can smoothly transport in the frame work while phonons are scattered by guest atoms. Particularly, in type-I clathrate compounds, guest atoms vibrate in a strong anharmonic potential because they are composed of a Weaire-Phelan structure, which divides a space with the maximum volume with the same cross-sectional area. While off-center clathrates such as type-I Ba₈Ga₁₆Sn₃₀, in which guest atoms vibrate in а double-well anharmonic potential, have low thermal conductivity, silicon-based clathrates are preferable for actual use in terms of the material cost.

In this study, we show that aluminum substitutions can enhance thermoelectric performance of silicon-based clathrates, type-I Ba₈Ga₁₆Si₃₀. Comparing calculated thermoelectric figure of merits (ZT) with those obtained in experiment, we concluded that (a) aluminum additive enhances ZT with lowering doping level and (b) further suppression of doping level can enhance ZT significantly (see Figure). To investigate thermoelectric properties, we obtained possible structures at finite temperature with using a cluster expansion and Monte Carlo method [1] and thermoelectric properties were averaged for different possible structures. Phonon properties of the clathrates were calculated with using a self-consistent phonon (SCP) theory based on first-principles calculations [2]. Our state-ofthe-art analysis method shows a good agreement with experimental data.



Fig. Temperature-dependent dimensionless thermoelectric figure of merit (ZT) of type-I Sibased clathrate with different carrier concentrations.

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First-principles calculations of multiferroic interfaces

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To obtain large magnetoelectric coupling in multiferroic materials, multiferroic interfaces are promising, because single-phase multiferroic materials exhibit typically antiferromagnetism preventing from having net magnetization [1, 2]. In addition to multiferroic interfaces, many types of magnetic interfaces are of fundamental importance to enhance the performance of magnetic materials. Nevertheless, our understanding from electron theory is far from being satisfactory. Since first-principles calculations of magnetic interfaces are computationally challenging, such study is also of importance in the sense of large scale computations.

In this project, we performed first-principles calculations of magnetic interfaces related with multiferroic materials [3–5] and permanent We demonstrated enhancemagnets [6-8]. ment of magnetoelectric coupling by insertion of Co atomic layer into $Fe_3Si/BaTiO_3(001)$ interfaces from first principles [3]. As is shown in Fig. 1, the interface Co monolayer helps the interface ferroelectric polarization exhibit enough, whereas the interface electric polarization is killed by Si without the Co monolayer at the interface. Other transition-metal monolayers are also investigated [4]. In addition, crystal-growth mechanism was also clarified for Co₂FeSi and Co₂MnSi films on singlecrystalline oxides by identifying the initial disorder at the deposition and the formation energy of random alloys relative to ordered alloy [5] by using both of OpenMX [9] and Akai-KKR [10]. Substantial progresses were obtained also for microstructure interfaces in permanent magnets [6-8].



Figure 1: Relative displacements $\Delta_{O-Ti} = z_O - z_{Ti}$ in the tetragonal BaTiO₃(001) film for each interface. For the Fe(Y)Si(Z) case, average values for Δ_{O-Ti} are shown. The first layer TiO₂(1) is the interface layer, whereas the fifth layer TiO₂(5) has the bulk atomic positions of BaTiO₃.

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Determination of the ionization energy and the electron affinity of organic molecular crystals from first-principles

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Ionization energy (IE) and electron affinity (EA) are fundamental quantities of organic semiconductors, and understanding the factors that determine the energy levels is of primary importance to the research and development of the organic electronics materials such as those of organic light-emitting diodes, organic fieldeffect transistors, and organic photovoltaics, dominating energy barrier for injection of a charge carrier (hole and electron).

IE and EA are measured with direct photoemission and inverse photoemission techniques, respectively. Notice here that the energy of the hole or electron injected into the sample is measured, i.e., IE (EA) is the magnitude of the energy difference between the neutral N-electron and the positively-(negatively-) charged N-1 (N+1)-electron systems. Thus, the measured IE and EA implies many-body interaction between the injected charge and the surrounding polarization clouds inside the organic solids which screen the injected charge. A complex of the injected charge and the surrounding dynamically induced polarization clouds are referred to as quasiparticles, which are theoretically well-described with the selfenergy determined by the many-body perturbation theory within the GW approximation.

Given an experimental measurement of a few organic monolayers on a substrate such as silica and graphite, it is of importance to investigate the electronic structure of an organic film of a few monolayer thickness with a reliable theoretical method. For such purposes, a periodic slab model approach is useful. To avoid the computationally demanding periodic slab calculation with GW, the electrostatic potential in a periodic slab was described within DFT-GGA, which was aligned to that in a bulk system. In the bulk system, the electronic polarization upon the injected charge was described within the GW approximation.

In this study, with a combination of the GW approximation suitable in general to solid or bulk systems and a periodic slab approach at the DFT-GGA level, I investigated polymorphs of pentacene (PEN) and perfluoropentacene (PFP). I theoretically demonstrated that the IE and EA at the surface are dominated by the electronic polarization (E_p) upon the injected charge induced by the surrounding polarization clouds, and the electrostatic energy (S) crucially affected by the orientation of the molecule at the surface of the organic semiconductor[1].

The geometrical configurations of the organic semiconductor bulk was determined with the STATE program code, with the lattice constants fixed to the experimental values. For the crystal structure and the lattice constants, two typical polymorphs were considered: single crystal and thin film phases of PEN, fabricated on SiO₂ and graphene substrates, respectively, and, herringbone and π -stacking motifs for PFP, that were reported to grow on the SiO₂ and graphene, respectively. For the optimized crystal geometries, I estimated the E_p upon the excess hole and electron, based on the quasiparticle self-energy within the GW approximation. I used the modified version of the GW space-time code, which enables highly parallelized calculations.

The resulting ionization energy (I_s) and electron affinity (A_s) are displayed by horizontal dotted dashed lines in Fig. 1. Here, the electronic polarization E_p was obtained as half the difference between the crystalline fundamental gap and that in a gas phase, assuming that $E_p^+ = E_p^-$. The I_s and A_s change drastically when the molecular orientation at the surface is taken into account, and thus, the non-zero S^+ and S^- contribute. The calculated I_s and A_s are in agreement with experiments.

Overall, while $E_{\rm p}$, which is approximated by the charge-induced dipole interaction, is quantitatively described within the GW approximation, the present methodology of estimating the electrostatic contribution S seems to describe well the electrostatic nature of the molecular orientation dependence of $I_{\rm s}$ and $A_{\rm s}$ at the surface, i.e., the charge-quadrupole interaction^[2]. The method lacks description of the decreasing polarization at the surface which amounts to the change of the quantities by $\approx 0.2 \text{ eV}[3]$. Nevertheless, considering the huge computational cost involved in treatment of the slab within GW, the method is suitable for quantitative treatment of an organic semiconductor nano-scale thin film, which is required for nano-scale or sub-nanoscale control of the materials properties.

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(b) Perfluoropentacene (5 ML)



Figure 1: Determination of ionization energy $(I_{\rm s})$ and electron affinity $(A_{\rm s})$ for the pentacene and perfluoropentacene polymorphs. The experimental gas phase ionization energy (I_g) and electron affinity (A_s) are indicated by the horizontal dashed lines, and the thick horizontal solid lines indicate $I_{\rm s}$ and $A_{\rm s}$ at the crystalline surfaces. The vertical dashed lines display the polarization energies P^+ or P^- , which are comprised of the electronic polarization $E_{\rm p}$ displayed by the double-headed arrows and the electrostatic energies S^+ or S^- indicated by the thick one-headed arrows. For comparison, the ionization energy and the electron affinity without taking into account the molecular orientation at the surface, i.e. $S^+=S^-=0$, are shown by horizontal dotted dashed lines.

DFT Prediction of Bulk Rashba Effect in Multiferroic Oxide

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Based on *ab-initio* approach using massive parallel computer simulations, we studied Rashba effect, which causes spin splitting of bands through the spin-orbit interaction. This year, we focused on multiferroics — the materials which show both ferroelectric and antiferromagnetic orders — in order to investigate the particular Rashba effect emerging with the magnetic symmetry that contains spin-flipping symmetry operations.

Density-functional theory (DFT) calculations were performed using the VASP code with GGA+U method. BiCoO₃ crystalizes in the polar P4mm crystal structure in which the Co^{3+} (d^6) ion located at the center of the O_6 octahedron is significantly displaced toward the apical O ion, leading to a pyramidal coordination rather than an octahedral coordination. The magnetic symmetry with the C-type antiferromagnetic order (defined by magnetic space group P4'mm') keeps the spindegeneracy of bands at the high-symmetric \mathbf{k} points. As shown in Fig.1, we found that the characteristic "vortex-like" in-plane components of the spin texture of the Rashba effect developing around the Z point while the outof-plane spin component is negligible [1].

The magnetic symmetry can be reduced when the Co spins are canted with respect to the C-AFM configuration in the real space. We assumed the application of external magnetic field along the [100] direction, by canting two Co spins simultaneously. As a result, we observed a distortion of the energy isocontour along the k_y axis and a downward shift of the center of spin vortex.



Figure 1: Spin texture (shown by magenta arrows) and energy contour plot of the conduction-bottom band in the $k_z = 1/2$ plane (centered at the Z point) in BiCoO₃.

While the theoretical predictions in the present study call for future experimental confirmation, we speculate that this phenomenon can be rather common among the antiferromagnetic polar systems; in future works, one can explore the possibility of Rashba effects in various multiferroic systems, such as $BiFeO_3$ and $PbVO_3$.

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First-Principles Molecular-Dynamics Study of Structural and Electronic Properties of Covalent Liquids and Glasses under Pressure

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The investigation of the dynamic properties of covalent liquids and glasses under pressure is important from perspectives of geophysics as well as fundamental liquid-state science. For this purpose, it would be important to consider the stability of materials states under various conditions from the viewpoint of free energy. To accurately evaluate which state is most stable, the thermodynamic integration (TI) method has been used by calculating the free energy [1]. While the TI method based on firstprinciples molecular dynamics (FPMD) simulations can obtain the free energy with sufficient precision [2], the system size is severely limited by its high computational cost.

In order to handle adequate system sizes while retaining first-principles accuracy, we adopt an interatomic potential constructed by artificial neural-network (ANN) models trained by FPMD simulations. This study aims to establish a method for the precise evaluation of the free energy using the TI based on the ANN-MD simulations. To that end, we have calculated the size dependence of the melting temperature of rubidium as shown in Fig. 1 [3].

We successfully reduced the computational

cost of numerical integration in the TI method by using an ANN potential compared with FPMD-based TI calculations, while keeping first-principles accuracy. By comparing with the results by FPMD, we confirmed that the ANN-based TI method gives the free energy within the accuracy of less than 0.1 meV/atom with more than 100 atoms.



Fig. 1: Melting temperature T as a function of the number of atoms N.

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Elucidation of diffusion process of ionic species in organic solvent

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Further improvement of Li-ion batteries (LIB) is strongly expected still now. The performance of LIB depends on various factors, and optimizing transport properties of Li-ion is one of the most important items. The microscopic transport mechanism in organic electrolytes, however, remains unclear. To elucidate it, we have developed a genetic algorithm based optimized force field (FF) which achieves large-scale and long-time classical MD simulation.

Polarizable FFs such as AMOEBA and APPLE&P are potentially applicable to large scale simulation for LIB systems, but their reliability is not sufficient as they are. In order to optimize AMOEBA FF and mimic the thermodynamic properties obtained by revvdW-DF2 density functional for target systems, we made a framework of multi-objective genetic algorithm, in which not only relative potential energy but atomic forces on each atom from VASP are reproduced by TINKER.

Pure ethylene carbonate (EC) and EC with Li-ion systems were assessed. The dimension of parameter space to be optimized is 132, and more than 150 MD snapshots sampled from "9 EC" and "43 EC + 3 Li^{+} " systems were used as training set. "360 EC + n Li⁺" systems (from 0.1M to 3.0M) were used for production run. The initial generation was prepared from the original parameters of AMOEBA FF with 20% random noise. The parameter sets formed four groups with the evolution, and only one group survived at 60th generation. Some of them successfully reproduced the diffusion coefficient and density calculated by VASP. Not only the solvation structure of Li-ions but also potential of mean force (PMF) for detachment and attachment of EC were also reasonably described. The diffusion of Li-ion becomes slower at high concentration and it statistically turned out that the lack of free EC molecules decreases attachment/detachment events. The detailed results are prepared for publication.



Fig. 1: (a) Improvement of solvated structure.(b) PMF along detachment of EC (DFT and FF).

First-principles study on the stability of magnetic alloys

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Transforming crystal structures of materials by adding pressure, heat, or other elements is one of the fundamental approaches to discover novel physical properties. Recently, a new Z3-Fe(Pd,In)₃ crystal type structure, was discovered by Teranishi's group in Kyoto University [1]. The new structure was obtained by introducing a third element of In into L1₂-FePd₃, which is the thermodynamically stable phase of binary Fe-Pd systems. Although the addition of In might be the key behind this new finding, the physical aspects of In in stabilizing the new structure is unclear and cannot be understood deeply only through experiments.

In this study, we performed theoretical analyses for the stability of an In-doped novel Fe–Pd phase to check the systems' formation energies using OpenMX. The model structures for the calculations were based on the chemical composition ratio of Z3-FePd₃ obtained from experiments. The In sites were chosen by replacing Fe or Pd sites with a specialquasirandom-structure method implemented in the Alloy Theoretic Automate Toolkit [3]. We investigated stable sites for In in the Z3-FePd₃ structure by comparing formation energies which is illustrated in the figure. We found that an In stably occupies the Pd site rather than the Fe site. There are two different Wyckoff positions of Pd labelled by 2e and 2g in Z3-FePd₃. From detailed analyses, we concluded that the new Z3-type Fe(Pd,In)₃ structure, in which a Pd atom at a 2e site is replaced with an In atom, is more stable than In-doped $L1_2$ -FePd₃ structures. These results are consistent with the experimental results from XRD, EXAFS, and STEM-EDS analyses.



Figure : The comparison of the formation energies of In-doped Z3- and $L1_2$ -type FePd₃.

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Electrode Properties of Novel Lithium-Ion Secondary Battery Materials: First-Principles Calculations

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We have studied electrode properties of Liand Na-ion secondary battery materials by first-principles calculations. The computations are done by using HiLAPW and Quantum Espresso codes.

X-ray absorption spectra in $NaFeSO_4F$ for exploring Na-ion battery reactions

We study electronic and spectroscopic properties of NaFeSO₄F, which has been a candidate cathode material for Na-ion batteries [1, 2]. NaFeSO₄F have been often synthesized experimentally from NaF and FeSO₄, and the calculated result shows that NaFeSO₄F is slightly stable in energy than the two-phase mixture of NaF and $FeSO_4$. The average voltage of NaFeSO₄F cathode is calculated to be 3.08 V with respect to the Na anode, and that comes dominantly from valence changes as Fe^{2+}/Fe^{3+} in NaFeSO₄F/FeSO₄F. X-ray absorption spectra (XAS) near K-edges at Fe, Na, and F are calculated for NaFeSO₄F and FeSO₄F as the cathodes in fully-discharged and fully-charged states, respectively, and also for NaF and FeSO₄ as possible residual materials in real cathodes (Fig. 1). The results show that XAS near K-edges, especially at F as well as Fe, provides us useful information to clarify battery reactions and structures in the cathodes.

O-redox and O₂-release reactions in Liexcess cation-disordered rock-salt oxides $Li_{2+2x}Mn_{1-x}Ti_{1-x}O_4$

The cation-disordered rock-salt oxides $Li_{2+2x}Mn_{1-x}Ti_{1-x}O_4$ with the Li-excess

amount x are one of promising Li-ion battery cathodes. We study the cathode properties of the $\text{Li}_{2+2x}\text{Mn}_{1-x}\text{Ti}_{1-x}O_4$ models (Fig. 2) with x ranging from 0 to 0.3 by the first-principles calculations, considering cation and anion redox reactions with O_2 -releases [3]. Effects of x on voltage-capacity curves and electronic structures are studied, and the results show that Mn-redox reactions predominate in early charging processes. As charging reactions further proceed, O-redox reactions contribute to the cathode reactions more significantly for higher x. From the formation energy analyses, it is found that O atoms tend to be released from the cathodes especially in late charging processes with a trend of easier O_2 -release for higher x, possibly accounting for lower experimental capacities than the theoretical values.

Na-ion battery performance and reaction mechanism of SnS anode

We study the Na-ion battery performance of SnS as an anode material by the firstprinciples calculations [4, 5]. From formation energy analyses, the discharge reaction processes of the Na/SnS half-cell system are clarified. We calculate the phase diagram of Na– Sn–S ternary systems by constructing convexhull curves of Na–Sn–S, and show a possible reaction path considering intermediate products in discharge reactions. Voltage-capacity curves are calculated based on the Na–SnS reaction path that is obtained from the ternary phase diagram. It is found that the conver-



Figure 1: Calculated x-ray absorption spectra (XAS) near Fe and F K-edges of NaFeSO₄F materials [1]. Experimental XAS is also plotted with the upper energy scale.

sion reactions and subsequently the alloying reactions proceed in the SnS electrode, contributing to its high capacity compared with the metallic Sn electrode, in which only the alloying reactions progresses stepwise. To confirm the calculated reaction process, x-ray absorption spectra (XAS) are calculated for Na₂S and SnS in discharged and charged states, respectively.

Conversion-type reaction mechanism of FeF_3 cathodes for Li-ion batteries

The perovskite-type FeF₃ is one of promising cathodes for Li-ion batteries because of its high capacity, but reaction mechanism has not been clarified yet. In this work, we study discharge reaction processes by calculating formation energies of Li–Fe–F materials. We theoretically find that the discharge reaction proceeds as FeF₃ + 3Li \rightarrow Li_{0.5}FeF₃ + 2.5Li \rightarrow FeF₂ + LiF + 2Li \rightarrow Fe + 3LiF, showing



Figure 2: Calculated model structures of $\text{Li}_{2+2x}\text{Mn}_{1-x}\text{Ti}_{1-x}\text{O}_4$ [x = (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3] with the cation-disordered rock-salt structures [3].

the insertion and the conversion reactions at early and late discharging processes, respectively. Based on the estimated reaction formula, voltage-capacity curve is calculated, and the result well accounts for the experimentally observed two-plateau behavior.

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First-principles study of quantum transport in nanostructures

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1 Introduction

An understanding of the electron transport properties of materials has resulted in the emergence of an important and versatile problem, not only for the fundamental research of science but also for the applications of electronics. Quantum nature is essential in nanoscale systems, and atomistic analysis based on detailed electronic states calculations are indispensable to discuss the transport property. In order to investigate transport properties, we have developed the nonequilibrium Green's function (NEGF) method, and the O(N) time dependent wave-packet diffusion (TD-WPD) method on the basis of the density functional theory (DFT). Using these methods, we have investigated charge, head and spin transport properties of materials. [1, 2]

2 O(N) method for transport calculations

Organic semiconductors have attracted much attention for their applications to flexible, printable, lightweight, and low-cost electronic devices. They are crystals that are assemblies of π -conjugated molecules weakly bonded by van der Waals interactions, and single crystallization has been achieved, enhancing the mobility. It is expected that the mechanism of carrier transport in organic semiconductors can be elucidated and that materials exhibiting high mobility can be developed by novel molecular synthesis.[3]

We developed the O(N) TD-WPD method for the quantum transport calculation of huge systems of up to 100 million atoms a decade ago.We calculated the conductance and the



Figure 1: Temperature dependence of mobility along the column direction in a C10-DNBDT single crystal. For comparison, the experimental values of FET mobilities are also shown as triangles.

mobility of the system with micron-order lengths at room temperature at the atomistic levels. Using this method we can study the transport properties from diffusive to ballistic regimes including the effect of realistic electron-phonon scattering, and determine the mean free path and relaxation time from an atomistic viewpoint. We performed DFT calculations of electronic structures and interactions between molecules of single-crystal organic semiconductors including the effect of the van der Waals interaction, and applied the TD-WPD method to the analysis of transport properties of the organic semiconductors.

Using TD-WPD method, we have proposed a prediction methodology to obtain charge transport properties of organic single crystals from their structural formula. Prediction of material properties of newly designed molecules is a long-term goal in organic electronics. As a demonstration, we employ the promising molecule C10-DNBDT. We succeeded in quantitative evaluation of charge mobility of the single crystal using our quantum wave-packet dynamical simulation method. Here, the single-crystal data is computationally obtained by searching possible packing structures from structural formula of the molecule. The proposed methodology can be a theoretical design technique for efficiently developing new high-performance organic semiconductors, since it can estimate the charge transport properties at early stage in the process of material development.[4]

3 NEGF-DFT method

We have developed a Simulation code for Atomistic Kohn-sham Equation (SAKE) for the ab-initio electron transport calculation based on the DFT and NEGF formalism.[5] We have applied the method to analyses of thermoelectricity of magnetic semiconductors.

Thermoelectric materials have attracted considerable attention from viewpoints not only of materials science but also of applications for energy harvesting by waste heat, and intensive works have been devoted to enhance conversion efficiency from thermal energy into electricity. The efficiency is expressed as a function of the figure of merit $ZT = \sigma S^2 T / \kappa$, where σ, S, κ and T are the electrical conductivity, the Seebeck coefficient, the thermal conductivity and the temperature, respectively, and the thermoelectric power factor is written as σS^2 . Enhancement of thermoelectric efficiency is not an easy task since the Seebeck coefficient, the electrical conductivity, and the thermal conductivity are not independent of each other. There is the trade-off between σ and S, and materials with high electric conductivity tend to have high thermal conductivity.

We analyze the thermoelectric properties of a magnetic semiconductor using SAKE program. The electronic transport properties, Seebeck coefficient, and the figures of merit are estimated for doped systems and thin films. We theoretically demonstrate the enhancement in the figure of merit by doping, which is in agreement with experimental work, and show further enhancement by the optimized doping. Furthermore, electronic structures of thin films are examined. It is shown that calculated electrical conductances reach to twice larger than that in the bulk, and the calculated Seebeck coefficients in thin films are suppressed by the metallicity, remain maximally to about a half of the results in the bulk.[6]

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Prediction of properties of organic ferroelectrics and piezoelectrics by first-principles calculation

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Organic charge transfer complexes show a variety of crystal structures and electronic properties. Among them, there is a class of compounds called "mixed-stack compounds", in which electron-donor and electron-acceptor molecules stack alternatively along a certain direction. Some of them show ferroelectricity. Tetrathiafulvalene-p-chloranil (TTF-CA) is a typical example. Kobayashi et al. successfully measured spontaneous polarization in TTF-CA and obtained a value of 6.3 μ C cm⁻² [1]. Furthermore, they found that the polarization value is more than 20 times larger than that of the point charge model, and their directions are opposite. To clarify the origin of this exotic ferroelectricity in TTF-CA, we made theoretical analyses in terms of Born effective chares as well as maximally-localized Wannier orbitals [2, 3]. We have shown that only 2 bands below the band gap are responsible for the emergence of polarization and also that the electron flow from cell to cell on these electronic states is the origin of the exotic polarization in TTF-CA.

Recently, Mezzadri et al. reported the structure of the low-temperature of 3,3,5,5-tetramethylbenzidinephase tetracyanoquinodimethane (TMB-TCNQ) and pointed out that this phase is potentially ferroelectric [4]. Similarly to the TTF-CA case, TMB and TCNQ molecules stack alternately and form one-dimensional columns. We have applied the above-mentioned computational methods to investigate the ferroelectricity in TMB-TCNQ and found similarities and dissimilarities with TTF-CA [5].

In addition, theoretical calculations to obtain spontaneous-polarization vectors for organic ferroelectrics D22bpy-Dia and D55dmbp-Dia have been performed. The obtained results explain the experimentallyobserved values well [6].

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Analysis of metal/oxide interfaces with large mismatches

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Metal/oxide heterointerfaces are widely used in engineering, and their microstructures govern the macroscopic properties. We investigated the interaction and bonding reconstruction at Pd/ZnO {0001} interfaces with large mismatches by density functional theory calculations combined with atomic-resolution scanning transmission electron microscopy. It has been believed that the interfacial interactions are very weak at incoherent interfaces with large mismatches, and metal–oxide interfaces can be more favorable than metal–metal interfaces.

To gain insight into the local atomic structures of each interface, first-principles calculations were performed using the Vienna ab initio Simulation Package (VASP). The electronic wave functions were expanded by plane waves up to a kinetic energy cutoff of 400eV. The generalized gradient approximation in the form of the Perdew–Burke–Ernzerhof exchangecorrelation functional was implemented in our calculations. A supercell containing seven Pd lattices matching six ZnO lattices along the interfaces was constructed to compensate the mismatch which agree with the experimental result. The surface atoms of the ZnO slabs were passivated by H atoms to eliminate the effects of dangling bonds, and a 15Å vacuum area was embedded into the outer Pd surfaces to avoid unwanted interactions. For k-point sampling, a $1 \times 1 \times 1$ Monkhorst–Pack grid was applied in the irreducible Brillouin zone for the supercell calculations. Convergence with a $2 \times 2 \times 1$ Monkhorst–Pack mesh was also tested for both interfaces, and the differences in the total energy and atomic configurations could be neglected. The convergence threshold for self-consistent iteration was set at 1.0×10^{-4} eV/atom, and the atomic positions were fully relaxed until the maximal force on each atom was less than 0.05 eV/Å. To analyze the interfacial stability of the epitaxial systems, the adhesive energy was calculated by $E_{\rm ad} = [E_{\rm Pd-slab} + E_{\rm ZnO-slab} - E_{\rm total}]/A$, where $E_{\text{total}}, E_{\text{Pd-slab}}, \text{ and } E_{\text{ZnO-slab}}$ are the interfacial total energy and the energies of individual Pd and ZnO slabs, respectively, and Ais the interfacial area. Then, we get $E_{\rm ad} =$ 2.66J/m^2 and 3.52J/m^2 for the Zn-terminated Pd (111)/ZnO (0001) and $(000\overline{1})$ interface, respectively, implying that the nonstoichiometric Zn-terminated Pd $(111)/ZnO (000\overline{1})$ interface is energetically favorable. The interfacial atoms were located almost at bulk lattice points for the stoichiometric Zn-terminated Pd(111)/ZnO(0001) interface while the interfacial Pd and Zn atoms underwent relatively large relaxations at the nonstoichiometric Zn-terminated $Pd(111)/ZnO(000\bar{1})$ interface, making the interface relaxed to release the large interfacial mismatch. The Pd-Zn bonds exhibited site-dependent characteristics and gradually transitioned from covalent to ionic at the Pd(111)/ZnO(0001) interface, whereas most of Pd-Zn bonds exhibited strong covalent behavior at the $Pd/ZnO(000\overline{1})$ interface [1].

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Firefly Oxyluciferin Anions in Aqueous Solutions

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Oxyluciferin anion, known as a light emitter in the firefly bioluminescence process, is a key molecule in understanding the mechanism of the firefly bioluminescence process. Although significant effort has been taken in various studies targeting the oxyluciferin anion, most of its properties still remain unclear. This is because, from the perspective of simulations, the environmental conditions surrounding the oxyluciferin anion are too complicated. In addition, the oxyluciferin anion is too sensitive for the environments.

In this study, we applied the first-principles Born-Oppenheimer molecular dynamics simulations (BOMD) to three possible isomers of the oxyluciferin anion (see Fig. 1) surrounded by 64 water molecules, and simulated the photoabsorption spectra for 1000 randomly selected molecular geometries from the trajectory [1].

The simulated spectra are in a good agreement with the experiments. The remaining error is less than 0.1 eV in comparison with the peak top positions. Our full QM simulations indicated a charge leakage from the oxyluciferin anion to the surrounding water molecules. In addition, we discussed the validity of a modeled aqueous solution, such as QM/MM or PCM methods, in which the charge transfer between solute and solvent is restricted. In order to describe the charge leakage from the oxyluciferin anion and reproduce our full QM results, at least 10 water molecules should be included into QM region.



Fig. 1. Three possible isomers of the oxyluciferin anion.

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First-principles investigation on electronic structure modulation via coherent phonon excitation

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Recent progress of coherent light source technology allows us to observe quantum dynamics in time-domain (TD) driven by intense and short laser pulses [1,2], rather than frequency-domain (FD) observation such as the standard spectroscopies. The TD information usually contains more than complementary information of FD data because of phase information, namely time-origin is clearly introduced by the pulse. Very recently, more extreme and flexible pulse shaping is available such that two-color mixing pulse composing infrared (IR) and ultraviolet (UV) photon energies. We have investigated coherent phonon excitation encoded in temporal modulation in angle-resolved photoemission spectra (ARPES) by using IR pump and UV probe pulses.

We observe TD-ARPES of Ta₂NiSe₅, a candidate of the excitonic insulators, pumped by 1.55 eV pulse. In the time-dependent E-k spectral distribution S(E,k;t), oscillatory behaviors appear. The frequencies of the oscillation well coincide with the optical phonon frequencies belonging to Ag irreducible

representation, all-symmetric, modes. These invoke that electronic results structure modulation due to the optical phonon, excited as coherent phonon via the IR pump pulse. Each part of the energy-dispersion has a different coupling with the phonon modes. By extracting a frequency structure $|S(E, k; \omega = \omega_{\text{phonon}})|$, much finer information of electron-phonon interaction than Raman spectra is expected to be extracted. To prove this scenario, we perform an that band structure ab-initio simulation modulation due to the optical phonon modes within the density-functional theory (DFT) framework within the abinit code.

Firstly, we optimize the atomic position of the Ta₂NiSe₅ crystal with two functionals, Perdew-Wang local density approximation (PW-LDA), and Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA). Secondly, we obtain normal modes of the lattice vibration at Γ -point via density-functional perturbation theory (DFPT) with each functional. By performing symmetry operations of the crystal, we assign irreducible representation to

the modes. We only pick up Ag irreducible representation because this mode is only excited as the coherent phonon based on displacive excitation of coherent phonon mechanism. The DFPT computation demands the heaviest computational resource. Our crystal is a semimetal with PW-LDA and PBE-GGA functional. To capture small Fermi surface, we need fine Brillouin zone sampling that has 864 *k*-points. The existence of Ta requires rather high energy cutoff, 50 eV, for the plane wave. The calculation takes 11 hours with 64 nodes, 1536 cores in the system B. Finally, we evaluate band dispersion with distorted atomic positions along with the normal modes obtained by DFPT. To compare with the experimental spectra, we construct similar spectral information as differences of k-resolved density-of-state (k-DoS) between the optimized atomic position and the distorted ones. The comparison between experimental and theoretical data shows an agreement that a symmetry breaking mode, having 2 THz frequency, shows the most

prominent change around Fermi-level of the spectra [3]. This mode has been argued as the driving mode of insulator-metal (IM) transition via photoexcitation. Our investigation posts an additional clue to understand the mechanism of the IM transition.

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first-principles calculation of exchange coupling constants and investigation of interface magnetism for various phases and their interfaces of permanent magnets

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Improvement of Nd-Fe-B magnets without heavy rare earth elements is one of the topics of increasing importance in the applied physics and materials science. The key for high-coercivity Nd-Fe-B magnets lies in the Nd-rich grain boundary (GB) phases [1]. However, the details of structural and magnetic properties of those GB phases are not clarified yet. Some experiments revealed the relationship between the crystallinity of GB phases and the relative angles between the interfaces and the c-plane of neighboring grains [2], which indicates the complexity of the physics in grain boundary phases in Nd-Fe-B magnets. Particularly, we targeted the exchange couplings inside and between the various phases for a computational study of magnetism in Nd-based permanent magnets.

For this purpose, we developed "jx", a postprocess program for OpenMX [3] to calculate exchange coupling constants between atoms based on the Liechtenstein formula [4]. The details of the implementation is explained in the published paper of [5]. During the development of jx, we found a remarkable problem about the combination of the Liechtenstein method and the linear combination of atomic orbitals (LCAO) approximation. When adopting diagonal elements of non-orthogonal (NO) Hamiltonian as effective single-site potentials, the calculated exchange coupling constants do not converge as increasing the number of basis. Figure 1(a) shows the exchange coupling constants J_{ij} as functions of atomic distance r_{ij} for different choice of basis sets. Here, the notation sxpydzfw means that the basis set is constructed from x types of s orbitals, y types of p orbitals, z types of d orbitals, and w types of f orbitals. It is possible to see in Fig. 1 that the J_{ij} profiles are similar for s2p2d1, s2p2d2, and s3p2d2 with fluctuations of about a few meV, whereas the J_{ij} profiles deviate strongly to negative values for the larger basis sets.

To solve this problem, we introduced a new scheme to orthogonalize the atomic orbitals, namely the single-site orthogonalization (SO) scheme. In the SO scheme, we derive a basis set $\{|i\rangle_i\}$ to orthogonalize only *i*-th element from the original non-orthogonal orbitals $\{|i\rangle\}$. The single-site orthogonalized basis set is defined by the following equations:

$$|i\rangle_{i} \equiv |i\rangle - \sum_{j\in\bar{i}} |j\rangle [\mathbf{S}_{\bar{i},\bar{i}}^{-1} \mathbf{S}_{\bar{i},i}]_{ji} \qquad (1)$$

$$|j\rangle_i \equiv |j\rangle, \ j \neq i$$
 (2)

with the definitions of the neighbor set \overline{i} for site i as

$$\overline{i} \equiv \{j \mid j \neq i, \ \langle i \mid j \rangle \neq 0\}.$$
(3)

We found that the J_{ij} profiles calculated with the SO scheme exhibit a convergent behavior as increasing the number of bases, while they



(d) negative J_{ii} in the ab interface model

Figure 1: Calculated exchange coupling constants J_{ij} of various systems. (a) J_{ij} of bcc Fe as functions of atomic distance r_{ij} for different choices of basis sets when adopting diagonal elements of NO Hamiltonian as effective singlesite potentials and (b) when adopting diagonal elements of SO Hamiltonian as effective singlesite potentials and applying the spin population scaling to the SO results. (c) and (d) J_{ij} in the ab interface model of Nd-Fe-B permanent magnet. decreases slightly depending on the basis size. The slight decreases in SO results are well collected by introducing spin population scaling, namely single-site orthogonalization with spin population scaling (SOS) scheme:

$$J_{ij}^{(\text{SOS})} \equiv \frac{\Delta n_i}{\Delta n_i^{(\text{SO})}} \frac{\Delta n_j}{\Delta n_j^{(\text{SO})}} J_{ij}^{(\text{SO})}.$$
 (4)

where $J_{ij}^{(SO)}$ is the exchange coupling constant derived by the SO scheme, $\Delta n_i^{(SO)}$ and $\Delta n_i^{(SO)}$ are the spin population at site *i* calculated using the NO basis and SO basis, respectively. Figure 1 (b) shows the exchange coupling constants as functions of atomic distances calculated with the SOS scheme. We can see a remarkable convergence as increasing the number of bases in Fig. 1(b).

We also applied the newly developed scheme to larger scale systems. Figures 1(c) and 1(d) show the calculated exchange coupling constants of the model of ab interface, where the amorphous Nd-Fe phase of a few nm are attached to the main phase in ab axis direction. It can be seen in Figs. 1(c) and (d) that the exchange coupling constants behave differently in the main phase and in the amorphous Nd-Fe phase.

We are now preparing the submission of the above results to refereed papers, and modified patch of jx including the SOS scheme for future release of OpenMX.

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Machine-learning-driven molecular simulations for grainboundary atomic dynamics

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Grain boundaries (GBs), crystalline interfaces between misoriented grains, often govern material properties in polycrystals, in spite the fact that changes in atomic arrangement and chemical composition occur within few nanometers from GBs. Experiments with bicyrstals and theoretical calculations have reported that not only atomic arrangements but also local properties arising from atomic dynamics significantly vary with each GB. Such properties includes thermodynamic stability, diffusivity and thermal conductivity. A better understanding of the connection between GB structures and their atomic dynamics is thus essential for designing polycrystals with desired properties and functionalities.

In order to reveal their connection, densityfunctional-theory (DFT) calculations have been often employed. However, DFF calculations are computational demanding as the number of atoms in a computational cell increases, since their computational time typically grows with $O(N^3)$ or O(NlnN). Due to this drawback, most DFT studies have investigated only GBs with simple atomic arrangements, such as symmetric tilt GBs with low Σ values. Still less is known about general or random GBs, which generally require a large number of atoms for their computational cells, in the atomic level.

In order to predict atomic structure and energetics of GBs while maintaining high accuracy and low computational cost, we constructed artificial-neural-network (ANN) interatomic potentials trained with DFTcalculation data, Furthermore, we integrated the ANN potentials into molecular simulation algorithms, with the goal of predicting local diffusional and lattice vibrational properties at GBs. Here, oxide systems and semiconductor compounds were chosen.

The architecture of ANN potentials was based on the previous studies by Behler [1]; the feedforward network was employed. Atomic environments were encoded using two- and three-body symmetry functions [1]. Their cutoff radii were set to 5 and 7 Å for oxides and compound semiconductors, respectively.

Training datasets were generated by accounting for various atomic environments to increase the generalizability of ANN potentials. Here the training datasets contained not only single-crystal structures but also lattice defects:

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point defects, surfaces and grain boundaries. DFT total energies and atomic forces were used to train ANN potentials. DFT calculations were performed using the VASP code [2].

Figure 1 and 2 show the error of total energies and atomic forces with respect to the reference DFT data in the training dataset for Al₂O₃ and PbTe, respectively. A data point distributed near the black dashed line indicates that the ANN potential accurately learns the training data without large error. These figures show that all the data points are distributed near the diagonal line, without large deviation, for both total energies and atomic forces. Thus the ANN potentials accurately learn the reference DFT results even for GBs.

The trained ANN potentials were then integrated into a structural optimization algorithm and molecular dynamics (MD) simulations to predict energetically favorable atomic arrangements at GBs not included in the training dataset. Figure 3 shows an example of Al_2O_3 GBs. The obtained structure was in agreement with an experimental observation and a theoretical calculation in the literature [3], demonstrating excellent predictive ability of our ANN potential even for GBs.

Finally we examined computational time of ANN-MD simulations. The computational time was found to linearly increase with the number of atoms. Ultimately, MD simulations with 10⁴ steps was finished in an hour even for GB structures with several thousands of atoms.



Fig. 1 Error of total energies and atomic forces with respect to the reference DFT data for (a) Al_2O_3 and (b) PbTe.



Fig. 2 GB structure obtained from molecular simulations with the trained ANN potential for Al_2O_3 .

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First-principles study on controlling of electronic structures and electron-transport properties of low-dimensional materials

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Recently, there has been a lot of energetic research and development of devices using low-dimensional materials. In the firstprinciples investigations, to estimate electrontransport properties of the nanoscale materials suspended between semi-infinite electrodes, self-energy matrices of the electrodes are required. The computational cost for obtaining the self-energy matrix is proportional to the cube of the lateral length of the electrode which is a direction perpendicular to the transport direction. Therefore, the computational cost increases dramatically as the system size increases.

In this subject, the method to calculate the self-energy matrices without any approximations and accuracy deteriorating is proposed. [1] In most cases, the electrode has a supercell structure in which a primitive unit cell is repeated in the lateral direction. Exploiting the repetition, the proposed method calculates the self-energy matrices of a large electrode by extending the self-energy matrices of the primitive unit cell using the singular-value decomposition. This makes it possible to greatly reduce the computational costs because calculating the inverse of a large matrix (for the supercell structure), which is the most computationally expensive, can be replaced by that of the small matrix (for the primitive unit cell). Furthermore, by comparing the self-energy matrix directly obtained from the large-sized electrode structure with that obtained using the proposed method, it was confirmed that the self-energy matrices can be reproduced without deterioration in the accuracy.

For demonstration of the proposed method, the computational time in generating the selfenergy terms for several supercell models is examined. For generating the self-energy terms, the computational time increases proportional to N^3 where N means the number of the total grid points in the supercell. In some cases, the computational efficiency exceeds the theoretical value (the square of the supercell size) because the order of the computational time for the recursive iteration to generate the selfenergy terms is slightly larger than N^3 . On the other hand, the computational time for reproducing the self-energy terms is notably reduced by the proposed method, and this benefit becomes more remarkable as the supercell size increases. These works have been performed on System B and System C.

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Elucidation of Reaction Mechanism of d-sorbitol Dehydration in High Temperature Water with Metadynamics

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1 Introduction

Chemical reactions in high temperature pressurized water without organic solvent or poisonous materials such as metals are worthy of attention with respect to environmentally friendly chemistry, i.e., Green Chemistry. In this study metadynamics calculation was achieved to elucidate the reaction mechanism for the cyclodehydration of sorbitol (SBT) [1] (Fig. 1) in high temperature water (HTW). Reaction pathways were searched on the free energy surface (FES) and the activation barriers were compared with the experimental values.

2 Method

In Metadynamics (MTD) simulations chemical reactions that do not happen in a regular time scale of molecular dynamics simulations are induced by adding a bias potential proportional to the appearance frequency on the FES defined with collective variables (CV). Bias potential at time t is expressed by a Gaussian function (equation (1)) with height h and width w_i , where $w^{-1} = \{1/w_i\}$. Bias potential is the historydependent term given by the sum of Gaussian functions (hills) deposited along the path followed by the fictitious particle (s_k) on the FES until time t. Sampling is effectively achieved by summing over N fictitious particles (walkers) which are allowed to move simultaneously on the FES. The point corresponding to the maximum accumulated potential and the point at the onset of the reaction correspond to the minimum point and the saddle point on the FES, respectively.



Fig. 1. The dehydration reaction of d-sorbitol (SBT).

$$V_{hills}(t, \boldsymbol{s}) = \sum_{\tau < t} \sum_{k=1}^{N} h \exp\left[-\frac{(\boldsymbol{s}_k(t) - \boldsymbol{s}_k(\tau)) \cdot \boldsymbol{w}^{-1}}{2}\right]$$
(1)

We used PIMD [2] to achieve MTD simulations associated with the Density Functional based Tight Binding (DFTB) method



Fig. 2. The reaction pathway and the collective variables (1,4-AHSO6).

using DFTB⁺ [3]. The present system contains one molecule of SBT, 30 molecules of H₂O, one proton and one Cl⁻ anion. The other system containing H₂CO₃ instead of H⁺ and Cl⁻ was also examined. The thermodynamic condition at 573 K and 20 MPa was the same as the experimental results [1]. Fig. 1 shows structures of SBT molecule and three products (1,4-AHSO, 2,5-AHSO and 1,5-AHSO) for the cyclodehydration of SBT. Considering the reaction pathway of cyclodehydration, there are two pathways for each product. CV is chosen for each pathway [4]. For example, there are two reaction pathways (1,4-AHSO3 and 1,4-AHSO6) for 1,4-AHSO depending on the position of OH group and the carbon atom involved in the reaction. Fig. 2 illustrates the pathway 1,4-AHSO6 and the associated CV. Here, the oxygen atom O3 in OH group on the carbon atom C₃ attacks the carbon atom C₆. In order to describe this reaction pathway the dihedral angle ϕ (O₆-C₆ -C₅-C₄) defined by the O₆-C₆ bond and the bond C₅-

C₄, the difference in the O-C bonds $d \ (= r_{O_3-C_6} - r_{O_6-C_6})$ between the O₃-C₆ bond and the O₆-C₆ bond, and the coordination number *n* of hydrogen atoms toward O₆ are selected as CV. The height of the Gaussian function was set as h = 500 K, and the step width of the variables are set as follows: $w_{\phi} = 10.0^{\circ}$, $w_d = 0.10$ Bohr, $w_n = 0.10$ and time step = 0.25 fs.

3 Results and Discussion

Over 3.6 ns of MTD simulations with DFTB along the pathway 1,4-AHSO6 the dehydration reaction was observed with the CV at $\phi = 155^{\circ}$, d = 0.0 and n = 2.1. Fig. 3 shows the calculated FES, where the shallow path was observed, leading to the transition state marked as the red arrow. With the Molecular Dynamics calculation started from this transition state as the initial state it was found that after the addition of proton to the oxygen atom (Fig. 4 ①) the dehydration (Fig. 4 ②) and the formation of a five-membered ring (C-O bond formation Fig. 4 ③) happened almost simultaneously. Hence, it is concluded that the hydroxyl group of SBT is protonated, the five-membered ring is formed via S_N2 mechanism, and finally the excess proton is released (Fig. 4 ④). This mechanism is the same as that for our previous study for the cyclodehydration of polyalcohol [4].



Fig. 3. The dehydration reaction of SBT to 1,4-AHSO6.



Fig. 4. The dehydration reaction of SBT to 1,4-AHSO6.

The activation energy with H^+ and Cl^- was lower than that with H_2CO_3 , indicating the activation energy has a negative correlation with acidity. However, relative relationship of calculated activation energies of products was not in agreement with the experimental results [1]. In order to overcome this problem, a method for smoothing FES was developed to decrease the sampling error and the calculation with this method is under way.

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Ab initio molecular dynamics study of stability of artificial retina molecule

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By means of ab initio molecular-dynamics simulations, we have investigated the light absorption properties in a photoelectric dye (2-[2-[4-(dibutylamino)phenyl 1 eheny]-3carboxymetheylbenzothiazolium bromide) (retina molecule) coupled to polyethylene. We adopted the Time-Dependent Density-Functional Linear-Response Theory (TDDFRT), proposed and formulated by Casida, for calculating lightabsorption spectrum. The absorption spectrum of retina molecule obtained by the simulation have a main peak at approximately 550, which is in the agreement with experimental result. Counterion substitution is considered one of the effective methods to improve the performance of retinal molecule. Figure 1 shows absorption spectra of the non-substituted retina molecule (counter ion = Br^{\cdot}) and substituted retina molecules (counter ion = F^- , Cl^- , I^-). The absorption spectra of the substituted system also have the main and small peak, and the profile of spectrum of I-substituted system is almost the same as non-substituted system. On the other hand, for F- and Clsubstituted system, the profiles of the absorption

spectra are different from that of non-substituted system in a sense that there are small peaks at longer wavelength region. In addition to halogen atoms, we also substitute Br with $[(CF_3SO_2)_2N]^-$ (TFSI) molecule, and investigated the stability and light-absorption properties. Our simulation found that substitution for TFSI molecule has the potential for increasing stability of the artificial retina. For absorption spectrum, the main peak is maintained, and no additional peak appears at longer wavelength region. Moreover, we have investigated effects of the water. Our simulation indicated that water stabilize the energy around the counter ion.



Fig1. Light-absorption spectra, inset shows spatial distribution of wavefuctions for HOMO and LUMO of non- and F-substituted system

Ab initio molecular dynamics study of structural properties and immiscibility of liquid Fe-Si-O mixtures under high pressure

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Liquid iron is a major constituent of Earth's outer core, but the core density is approximately 10 % lower than that of pure iron. Therefore, light elements (LE) such as hydrogen, carbon, oxygen, silicon, and sulfur are expected to exist in the core. Under this circumstance, we have studied the effects of light element on the structural and transport properties of liquid iron mixtures by means of ab initio molecular-dynamics simulations. For Fe-LE binary systems, we clarified the structural properties and interactions between LE atoms at core-mantle boundary condition [1]. The C-C interactions are stronger than those of other light elements. The S-S interactions depend on the S concentration, in the sense that the shape of pair distribution functions for the S-S correlation change with increasing S concentration. In addition to the binary systems, we have investigated the structural properties of liquid Fe-Si-O ternary systems. From the radial distribution function obtained from our simulations, it is found that Si and O atoms shows "substitutional" and "interstitial" behavior even in liquid Fe-Si-O ternary system. The interaction between Si and O

atoms is stronger than those between other atoms, which means that a covalent like interactions exists between Si and O under outer core conditions. Moreover, our simulation found that liquid Fe-Si-O ternary systems shows immiscible tendency under outer core conditions. Figure 1 shows atomic configuration of liquid Fe-Si-O at about 140 GPa obtained from our simulation. As shown in figure 1, oxygen atoms confined to the narrow area (red area in Fig. 1).



Fig1. Snapshot of the atomic configuration. Gray, yellow and red ball show Fe, Si and O atoms. Red area shows the area in which oxygen atoms exist.

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Construction of Neural Network Force Field for Molecular Dynamics Simulation in Multicomponent System

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In this study, we aimed to development of an interatomic potential using an artificial neural network (ANN) applicable to multicomponent systems such as life systems. This is one of the data-driven interatomic potential that takes advantage of ANN's universal function approximation, and automatically constructs a functional form that represents the input data through training. Since first-principles (FP) calculation data is mainly used for the training, molecular dynamics (MD) simulations with ANN potentials (ANN-MD) are expected to be accessible to large-scale systems or long-term calculations while maintaining FP accuracy. However, the current construction method may yield less robust ANN potentials, making longterm MD calculation difficult. Therefore, we first have investigated the factors affecting the robustness of ANN potential [1], where the ionconducting phase of α -Ag₂Se is employed as an example system.

The most important factor was found in training data. Generally, it is difficult to prepare highly diverse FP data due to its large calculation cost. However, minority data can be physically very important. That is the FP data with the interatomic distance approaching. Even if the interatomic distance approaches during ANN-MD simulation, the ANN potential does not learn such a state, thereby failing continuing the calculation. For long-term MD simulations, it was thus necessary to oversample such rare FP data and let ANN learn. (Actually, FP data for the relaxation process from the state where the atoms are close to each other is also needed.)

Next, we tried whether the key findings obtained the ANN through potential construction for α -Ag₂Se can be applied to the multicomponent systems. The amorphous glycine taken as an example is a system in which glycine molecules composed of four elements H, C, N, and O are irregularly aggregated, and proton transport occurs between the molecules. In the case of ANN potential without training rare FP data, the MD simulation cannot be continued for a few fs. When it is learned, at least ns order is possible. Although the glycine amorphous system is not a living system, we consider that this result is a great step forward.

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Manipulation the cross-plane thermal conductivity of the 2D hetero-junction materials

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We have studied the two-path phononinterference resonance which induces a stop band in silicon crystal matrix by embedded nanoparticles array [1] and the coherent phonon transport in van der Waals graphene-MoS₂ hetero-structure, using the massive parallel computer simulations.

Massive efforts have been devoted to control phonon transport in the phononic crystals utilizing phonon interference and in the phononic metamaterials (local nanostructures) utilizing local phonon resonance. However, since the phononic crystals require strict global periodicity and the local resonances in the metamaterials only affect phonons with specific discrete frequencies, further development of phonon engineering has been a pressing and baffling challenge. A new mechanism that can mitigate the strict requirement of the globally periodic nanostructure and can influence a broader and continuum range of frequencies (the stop band) is urgently needed.

We have studied a new stop-band formation mechanism that is the two-path phononinterference resonance by using the atomistic Green's function calculation and the wavepacket molecular-dynamics simulation. Compared with the traditional stop-band formation mechanism (single-path Bragg scattering), the two-path resonance mechanism has a significant advantage in not requiring the strict periodicity in nanostructures, due to the local origin of the phonon resonance.

Moreover, there are growing efforts to control thermal transport via coherent phonons in the one-dimensional superlattice. However, in general, the difference in the intrinsic lattice of the constituent structures materials inevitably generate interface disorder during the fabrication process, greatly limiting direct experimental observation of the coherent phonon transport. The flexible integration and atomistic interlayer smoothness of van der Waals hetero-structure provide an ideal platform for the coherent phonon transport manipulation. Thus, in the second work, using non-equilibrium molecular the dynamics simulations, we investigate the coherent phonon transport in van der Waals graphene-MoS₂ hetero-structure with different stacking order at room temperature. The histogram of the phonon transmissions in different

disordered structure exhibits a log-normal distribution, which reveals a localization of the coherent phonons. Furthermore, the optimal stacking order of the graphene and MoS2 is efficiently identified from tens of thousands of candidates by machine learning. The significantly suppressed of the phonon transmission in the low frequency (<5THz) phonons of the optimized structure lead to a significant reduction (~95%) of the thermal conductance compared with the pristine graphite. Finally, the effects of the temperature and strain effect on the thermal conductivity of graphite and optimized structures are also discussed. Our work provides a deep insight into the coherent phonons transport behavior in the atomistically smooth van der Waals structure, which is beneficial for further development of phononics.

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Development of algorithms in crystal structure prediction

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We have developed a crystal structure prediction tool, CrySPY as an open source software [1]. CrySPY is interfaced with VASP[2], Quantum ESPRESSO[3], soiap[4], and LAMMPS code for structure optimization. Several searching algorithms are available in CrySPY, such as random search (RS), evolutionary algorithm (EA), Bayesian optimization (BO), and LAQA. RS is a basic algorithm and widely used. EA[5, 6, 7] is currently very popular. We have implemented implemented EA into our CrySPY code. Previously we have developed selection-type algorithms with machine learning. BO can efficiently select potential candidates from a large number of candidate structures by machine learning[8]. LAQA is one of the refinforcement learning, which can reduce the computation time[9]. The key point here is that the selection-type algorithms are not exclusive with EA. In this study, we develop a hybrid algorithm of BO and EA. This hybrid algorithm could be the most promising way to find the global minimum structure in large and complicated systems. Moreover, we compare searching efficiency among the RS, EA, BO, and hybrid algorithm.

Searching efficiencies of RS, EA, BO, and the hybrid algorithm have been investigated in two systems of Si_{16} and Si_{32} . The former is a relatively easy system to find the most stable structure, and the latter is slightly difficult. For the system of Si_{16} , we optimized a hundred structures using interatomic potential calculations with the solap code in each algorithm. Here, a hundred structures were selected from three hundred structures particularly in BO and the hybrid algorithm. A hundred structures were obtained by random structure generation and the remaining two hundred structures were generated by EA in the hybrid algorithm. To statistically investigate searching efficiencies, we carried out simulations of crystal structure prediction 50 times. The success rates to find the most stable structure were 64%, 58%, 70%, and 82% for RS, EA, BO, and the hybrid algorithm, respectively. The success rates of RS and BO were slightly better than that of EA. Random structure generation is sufficiently effective to find the most stable structure in this small system. The number of searching trials (100 structures) might be too small for EA. The success rate of the hybrid algorithm was the highest in which we generated 200 structures by EA. This is because EA was able to generate good candidates and BO efficiently selected the good ones. For the system of Si_{32} , three hundred structures were optimized in each algorithm. In BO and the hybrid algorithm, three hundred structures were selected from six hundred structures. Three hundred structures were obtained by random structure generation and the remaining half of the structures were generated by EA in the hybrid algorithm. The success rates were 46%, 60%, 54%, and 74% for RS, EA, BO, and the hybrid algorithm, respectively. The success rate of RS was lower than others since the system became complex. Although the success rate of BO was better than that of RS, BO was not as good as EA. Random structure generation is no longer effective in this system. However, the success rate of the hybrid algorithm was still the highest. These results show the hybrid algorithm is superior to EA and BO and could be the most promising method for the crystal structure prediction.

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Large scale ab initio calculations on the fundamental processes of solar energy convergence devices and on designing principles for new materials

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1. Electron-phonon interactions in tungsten oxide photocatalysts

Water-splitting photocatalysts, which decompose water into hydrogen and oxygen by sunlight, are promising for a clean and renewable energy source for the next generation of hydrogen production. A considerable amount of literature has been published on the photoexcited state of tungsten oxide, and longlived trapped photocarriers have been found to play a key role in photocatalytic reactions. Using XAFS techniques, Uemura et al. found that the photoexcited electrons stay on the tungsten atom and the local structure is changed [1,2]. However, there has been no detailed investigation of the structural changes caused by photoexcited electrons and the changes in electronic states associated with these structural changes. In this work, electronic states, phonon, and electronphonon interaction calculations for tungsten oxide were performed by using rst-principles calculations based on density functional theory in order to discuss the lattice distortions caused by photoexcited electrons. ese calculations were performed by using Quantum ESPRESSO 6.3 and Yambo 4.2.4. GGA-PBE and "on the mass shell" approximation were used for these

calculations. An integral approach utilizing 500 random Q points was used for the electronphonon interaction calculations. e results showed that the bandgap of the direct transition at the Γ point is larger than the bandgap of the indirect transition. It is suggested that the bandgap of the indirect transition is more preferred and reduce carrier recombination. Next, the Eliashberg function was calculated to nd the phonons that contribute signi cantly to the electron-phonon coupling. e transition dipole moment on the Γ point of the structure, which is displaced in the direction of the strain caused by the phonon, was calculated. It is suggested that the strain caused by the phonon, which is strongly coupling with the electrons on the CBM, reduces the transition dipole moment, and also reduces the recombination of the photocarriers.

2. Device-Scale Simulations of Organic Photovoltaics for Performance Improvement

Organic photovoltaics, OPVs, are promising energy harvesting devices, but their power conversion efficiencies are lower than traditional silicon ones. For performance enhancement, it is important to control properties of donor and acceptor materials, such as HOMO and LUMO levels, by molecular design. Fullerene derivatives, *e.g.*, phenyl-C₆₁ butyric acid methyl ester, PCBM, have been used for acceptors, but recently non-fullerene acceptors are attracting attentions because of easiness of LUMO level tuning and light harvest. A non-fullerene acceptor is composed of three units: π conjugated core; alkyl side chains, which control solubility; and electron-withdrawing end groups, which control LUMO level. It is however challenging to synthesize and evaluate device performances for combinations of donors and acceptors.

In this work, density functional theory, DFT, code as implemented in NTChem was employed to evaluate material properties of donors and non-fullerene acceptor candidates. We implemented programs to generate NTChem inputs—Cartesian products of cores, side chains and end groups—from SMILES. HOMO and LUMO levels of indacenodithiophene, IDT, derivatives were evaluated at ω B97X-D/def2-SVP level of theory, which reproduces dependence of LUMO levels on electronegativities of end groups. In future work, it is planned to evaluate other properties such as electron mobilities, absorptions spectra, and exciton lifetimes.

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Computational physics and chemistry approach to develop the artificial photosynthesis and fuel cell catalysts

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TiO₂ is well known as an efficient photo catalytic material and has a wide range of application area from air-purifier to antimicrobial coating. However, TiO₂ uses only the ultraviolet ray which is less than 3 % of the whole sunlight pouring on the earth surface. Therefore extensive studies have been devoted to develop photo-catalytic materials sensitive to visible light that makes up 50 % of the sunlight.

A large number of double-perovskite oxides, $A_2B'^{III}B''^{V}O_6$, have been studied due to their intriguing physical and chemical properties originating in their mixed valence na-Above all, Ba₂PrBiO₆ was found ture. to show an efficient photo catalytic activity to dissolve water molecules into oxygen and hydrogen gases under the visible light. However, detailed theoretical analysis on the electronic structures and the crystal geometries of the double-perovskites has not been performed. In this work, we study the structural and electronic properties of Ba₂Bi^{III}Bi^VO₆, Ba₂PrBiO₆, and Ba₂PrSbO₆ double-perovskites using the first-principles density functional theory [1]. The Hevd-Scuseria-Ernzerhof hybrid functional was applied to the calculations to handle the strong electron-correlation.

First of all, we evaluate the structural and electronic properties of $Ba_2Bi^{III}Bi^VO_6$ as it gives the basis in analyzing the double perovskite crystals. Unit cell contains four $BaBiO_3$ chemical units where the Bi^{III} octahedra and the Bi^{V} octahedra are arranged alternately forming the *B*-site ordering. Where the distortions of octahedra caused by the mixed valencies are characterized by breathing distortion and tilting angle as depicted in Figure 1. We find that the Bi^{III} 6s states at the top of



Figure 1: Distorted octahedra of $Ba_2Bi^{III}Bi^VO_6$.

valence band of Ba₂Bi^{III}Bi^VO₆ vanish on the Pr substitution for Bi at B'^{III} -site. When Sb is substituted for Bi at B''^{V} -site, the Bi^V 6s states at the bottom of the conduction band vanish causing additional widening of the band gap. Further, our calculation suggests that the Ba₂PrPr_{Bi}O₆ is a possible candidate as a source of the Pr^{IV} signal observed in the experiment. We find that the anti-*B*-site atomic configurations, Ba₂ $B''^{V}B'^{III}O_6$, are easily restored to those of the original structures. This demonstrates the stability of the *B*-site ordering in the double-perovskite framework.

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Reveal the mechanism of thermal transport in PbS quantum dot system

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Colloidal quantum system has attracted a lot attention recently due to their controllable electronic and optoelectronic properties.[1] Therefore, the colloidal quantum dot systems are promising for a wide range of applications from solar cells, thermoelectric devices, photodetectors, and many others. [2] Understanding the thermal properties of such quantum dots system is crucial for the thermo-stability and the performance of the above-mention ap-However, due to the large unit plication. cell size and complex inter-atomic interaction, the thermo properties for such system is still less understood. In this project, we applied the molecular dynamics simulations to systematically investigate the thermal transport in PbS quantum dot system. The large-scale molecule dynamics simulations is carried out by the open source software LAMMPS with the computational resource from The Institute for Solid State Physics (ISSP) of the University of Tokyo.



Figure 1: Illustration of the non-equilibrium molecular dynamics simulation for thermal conductivity calculation in PbS ligand system The simulation model used for thermal properties calculations is shown in Fig.1. The size of the PbS dots is about 3 nm, which contains about 600 atoms. $C_5H_{10}S_2$ ligands are used to bridging the connection between the quantum dots. The length of the system range from 20-100 nm, while are cross-section of 10 nm × 10 nm with periodic boundary is used in the direction perpendicular to the heat flux. The simulated thermal conductivity from the nonequilibrium molecular dynamics simulations is as lower as ~0.1 W/mK at temperature of 300 K. As a reference, the thermal conductivity of bulk PbS is about ~5.0 W/mK based on the same interatomic potential.





To understand the origin of the lower thermal conductivity in such system, we calculated the spectral-resolved thermal conductivity at different temperature and the results are shown in Fig. 2. From this figure, we can clearly see that thermal transport in PbS quantum dots system is dominated by low frequency phonon in the frequency range of $0.2\sim5$ THz, while the high frequency vibrational modes are mainly scattered at the PbSligand interface. This explained the ultra-law thermal conductivity in such quantum dot system.

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Exploration of surface reactions on model real catalyst II

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This year, as in the previous year, we studied two chemical reactions on inorganic surfaces using density functional theory (DFT) utilizing parallel computational resources of ISSP's supercomputer system and the Vienna Ab initio Simulation Package (VASP) version 5.4.4. On top of that, we worked on the development of an electronic structure theory for quantum computing.

The first reaction was the industrially relevant Ziegler–Natta catalysis for olefin polymerization, which is based on titanium chlorides supported by MgCl2. In the previous year, we had revealed that two alkyl aluminum molecules are involved during the active-site formation process. This year, we examined three possible reaction paths of the active-site formation in detail, and found a new possible transition state.

The second reaction was a diffusion of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA), which is an organic semiconductor molecule, on the Ge(001) surface. In the previous year, we had located the transition state of this reaction using the climbing-image nudged elastic band method. This year, we

performed a detailed analysis of the reaction. It was found that the adsorption character transforms from the chemisorption with the physisorption at the reactant and product into the physisorption at the transition state during the diffusion.

In addition to the above two studies, we developed a new quantum chemical method for quantum computing based on the variational quantum eigensolver (VQE). The VQE is a quantum-classical hybrid algorithm to optimized wave-function, where quantumcircuit parameters are determined variationally. Our method, called orbital-optimized unitary coupled cluster doubles, optimizes both quantum circuit parameters and molecular which orbitals simultaneously, allows computing first-order molecular properties easily in the framework of the VQE. Taking advantage of this property, we realized the first geometry optimizations of polyatomic molecules using the analytical energy derivatives of the VQE.[1]

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DFT calculation of atomic displacements captured by energy dissipation of noncontact atomic force microscope

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In the last two decades the conservative and non-conservative (dissipative) force interactions between a tip and a sample in proximity have been examined by non-contact atomic force microscopy (nc-AFM). In particular, the channel of nc-AFM to measure the energy dissipation through the non-conservative force interactions has been regarded to have great potential to explore nano-mechanical phenomena; the dissipation channel gives the change in the amount of mechanical energy to maintain the constant oscillation amplitude of an AFM cantilever. We had experimentally found that, when the nc-AFM image showed the high resolution for the individual adatoms on a



Fig. 1: Simultaneously obtained nc-AFM image and the energy dissipation image, with the structure model of Si(111)-(7×7).

Si(111)- (7×7) surface, the simultaneously obtained energy dissipation signal increased in close proximity over the hollow sites surrounded by a Si adatom and a Si rest atom with a dangling bond per each (Fig. 1) [1]. Based on the experimental results, the dynamic atomic processes responsible for the dissipation had been discussed in regard to breaking of the backbonds of the Si adatom and subsequent bond formation in an alternative atomic configuration of the Si surface atoms, including the Si atom at the apex of AFM tip. In this study, to elucidate the phenomena, the surface diffusion potentials of a Si adatom were calculated using real-space density functional theory (RSDFT) [2] when the Si tip was brought closer to the Si(111)- (7×7) surface. RSDFT is a first-principles program developed by Oshiyama and Iwata, which uses a real-space difference method and a pseudopotential method.

First, we optimized the structure of Si(111)- (7×7) reconstructed surface consisting of 298 Si atoms and 49 H atoms by RSDFT, as shown in Fig. 2. Then, the surface diffusion potential for a

corner Si adatom was calculated from its original position to the neighboring hollow site (Fig. 3). The hollow site seems metastable because of a diffusion barrier from the hollow site to the adatom site, the barrier height of which was several tenth of 1 eV. Our preliminary calculations anticipated that the diffusion barrier is lowered and the adatom can move to the hollow site, when the tip is in close proximity to the surface [3]. It is deduced that the oscillating nc-AFM cantilever can provide the Si adatom with the kinetic energy to overcome the barrier



Fig. 2: Optimized atomic structure of Si(111)- (7×7) . (a) top view. (b) side view.

from the adatom site to the hollow site. This energy of less than 1 eV could be captured as a dissipation energy in the nc-AFM experiment.

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Fig. 3: Surface diffusion potential of the Si adatom from the original position (x = 0, denoted by Co (corner adatom site)) to the neighboring hollow site (x = 2.25 Å) without the Si tip.

Hybrid *Ab-Initio*/Machine-Learning Computation for Designing Nano/Molecular Structure

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Designing and developing functional materials/molecules often require vast searching of target properties from extra-large data set, which is far out of the capability of conventional computing algorithms. In recent years, the Deep-Learning (DL)-based molecular design methods have been extensively studied. One of the recent studies has reported [1] a machine learning method for predicting molecular properties by mapping a graph representation of a molecule to a latent variable space and by linking the variable to physical property of the molecule. Representing molecules in the latent space enables an efficient property search within existing data, because the DL model transforms the discrete representation of a molecular graph into a continuous variable space suitable for various numerical algorithms.

In the present study, we have developed a hybrid algorithm that combines the continuous representation of molecules with an optimization algorithm to predict physical properties of organic molecule [2]. Here the Grammar Variational Autoencoder (GVAE) [3] algorithm was adopted for transforming discrete representation of a molecular graph into continuous representation. The optimum value of the HOMO-LUMO gap obtained by an abinitio quantum-chemical calculation was predicted by searching a molecular structure within the latent space.

The input of GVAE is a Simplified Molecular Input Line Entry System (SMILES) string, which represents a molecular graph. The GVAE consists of two neural networks: An encoder and a decoder. The encoder converts SMILES into latent variables z, whereas the decoder converts z back to the original SMILES string. These neural networks are trained so that an input SMILES coincides with the output SMILES. The distance between molecules with

closer SMILES is mapped to a closer point in the latent variable space. By using this method, molecular design with desired characteristics can be treated as an optimization problem in a continuous variable space. We have examined the algorithm for predicting molecules using the Quantum Machine 9 (QM9) as a training dataset.



Fig. 1 The molecule and its properties predicted by the present method

Figure 1 shows the molecule possessing a targeted HOMO-LUMO gap among possible molecular structures with atomic species of C, O, N, F, and H, predicted by the present algorithm. In this case, CF_4 was predicted to have the widest gap of 0.62151 hartree among the possible molecular formula in the QM9 [2]. Parallelly, we have performed an *ab-initio* molecular dynamics study on water-molecule dissociation in a nanostructured perovskite material (MAPbI₃) [4]. These computations have been done in part by using the Supercomputing System at SCC-ISSP

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Analysis of ion conduction in materials of proton-conducting solid electrolyte and application to catalytic surface reaction with proton conductors

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1. Introduction

Ammonia has been regarded as one of the attractive energy carrier for storage and transport of hydrogen because of its high hydrogen content and high energy density. Electrosynthesis of ammonia from nitrogen and water has been studied as a novel process replacing the conventional Haber-Bosch process which consumes a lot of energy.

We reported electrosynthesis of ammonia using an electrolyzer cell with a protonconducting electrolyte and cathode catalyst of Fe and Ru. We found the ammonia formation rate is remarkably enhanced with increasing polarization cathode (electrochemical promotion effect)¹. Since dissociation of nitrogen triple bond is a rate-determining step in the ammonia formation reaction, we consider that the application of the cathodic polarization promoted the dissociation reaction of nitrogen triple bond.

As for the dissociation reaction of nitrogen molecule on the metal catalyst, previous studies based on theoretical calculations suggested majorly two different mechanisms for the N₂ dissociation reaction on a surface of the cathode catalyst metals^{2,3}. One is the direct dissociation mechanism in which nitrogen molecule adsorbed on the surface of the catalyst directly dissociate into two adsorbed nitrogen atoms. The other is associative mechanism in which hydrogen atom initially reacts with the adsorbed nitrogen molecule to form N₂H species and successive reaction with

hydrogen atom dissociate the nitrogen bond step by step. However, the roles of the cathodic polarization of the catalyst and protons supplied from the electrolyte on the nitrogen dissociation reaction in the ammonia electrosynthesis process are still unclear.

In this study, the roles of the cathode polarization of the catalyst and protons from the electrolyte are investigated by theoretical calculations based on density functional theory (DFT) to reveal the mechanism of the electrochemical promotion effect of ammonia formation reaction.

2. Computational methods

For the calculation of the surface reaction, a slab-and-vacuum model was employed. We chose BaCeO₃ (BCO) with a BaO₂-terminated (001) plane as a proton-conducting oxide slab and a Ru cluster on the surface of the BCO surface as a catalyst. DFT calculations were performed with VASP5.5.4 code. The generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (GGA-PBE) represented the exchange-correlation energy functional⁴. Plane-wave cut-off energy of 400 eV was adopted. Monkhorst-Pack *k*-mesh of $2 \times 2 \times 1$ centered at the Γ point for the geometry optimized supercells. To reveal the effect of the cathodic polarization on the nitrogen dissociation, density of states (DOS) of the systems with one nitrogen molecule apart from the catalyst and that with nitrogen molecule adsorbed on the catalyst were calculated. Moreover, one electron was added to the system with adsorbed nitrogen molecule to reproduce the cathodic polarization in the ammonia electrosynthesis.

3. Results

In the calculation for the model without adsorbed nitrogen, electron-occupied Ru 4d state was emerged at around Fermi level after the addition of an electron, which suggested that the cathodic polarization activates an electron-donating property of the Ru catalyst. Moreover, the calculation for the model with adsorbed nitrogen showed that an anti-bonding orbital of the adsorbed nitrogen located around the Fermi level after the electron addition. Then, charges of constituent atoms of the Ru cluster and the adsorbed nitrogen molecule (Fig. 1) were calculated for the system before and after the electron addition. As summarized in table 1, the N2 atom and the Ru atoms were negatively charged after the electron addition. These results suggested that back donation of electron from the Ru catalyst to the adsorbed nitrogen molecule can be promoted by the application of the cathodic polarization.

To clarify the possible nitrogen dissociation mechanism, the reaction activation energies for the two mechanisms were calculated with the nudged elastic band (NEB) method. Though the apparent difference in the activation energy was not observed, side-on configuration of the adsorbed nitrogen molecule was stabilized in the dissociative model by the addition of an electron. This result allows us to expect that the dissociation mechanism can be promoted by the cathodic polarization.



Fig. 1. The Ru cluster and the adsorbed N_2 molecule on the BCO (001) surface with BaO₂-termination.

Table 1. Calculated charges normalized by elementary charge for constituent atoms of the Ru cluster and the adsorbed nitrogen molecule before and after the addition of an electron normalized by elementary charge.

Atom	Before	After	Variation
N1	-0.36	-0.35	0.01
N2	-0.05	-0.15	-0.10
Ru1	-0.42	-0.51	-0.09
Ru2	0.16	0.07	-0.09
Ru3	-0.03	-0.09	-0.06
Ru4	0.09	0.04	-0.05

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Transport and reaction properties of nanographene

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1. A cross-correlation transport effect of a magnetic Ni/h-BN/Ni junction

We found that a thin magnetic Ni/h-BN/Ni junction allows a novel magnetoresistance effect controllable by the external electric-field, *i.e.* a cross-correlation effect. The effect comes from realization of local pyramidal B-N₃ structures of the h-BN monolayer. When the antiparallel spin configuration of two ferromagnetic Ni layers is fixed, the spin-polarized tunnel current is reversed in its spin-moment direction by the electric field whose field strength is within a realizable range. Switching upright pyramids to inverted pyramids, the electronic polarization direction in the h-BN layer and the spin-moment direction are reversed.[1]

2. The strong-correlation effect in an elastic property of defect-free graphite

We developed new DFT-based simulation methods, *i.e.* LDA+U+RPA and ACFDT-RPA+U, for the explanation of unexpectedly large elastic constant C_{33} of the defect-free monocrystalline graphite by KANEKA, which is measured by the microscopic picosecond ultrasound method.[2] The short-range correlation effect described by the U term causes unharmonic potential profile raising C_{33} from the value by ACFDT-RPA by more than 20%.

3. Hydrogen production catalyzed by graphene with vacancies

We found that hydrogenated graphene vacancies promote dehydrogenation processes of several alkane molecules in simulations. Based on these results, we can propose that creation of atomic vacancy becomes the activa-



Figure 1: Calculated C_{33} by LDA+U+RPA (solid line) and LDA+U.[2]

tion of the dehydrogenation catalytic property of graphene, which is shown to be realized in experiments.[3]

4. Zero modes in PTM molecules

The counting rule of zero modes by Morishita holds generally in a set of phenalenyl tessellation molecules (PTM).[4] Based on the ruled creation of zero modes, we can construct a certified ferrimagnetic Hubbard model in two dimensions. An effective low-energy model becomes a Kondo-lattice model, where extending orbitals causes the Kondo screening in localized spins of arrayed zero modes.

Acknowledgement

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van der Waals density functional study of image-potential states at organic-metal interfaces

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Recent progresses in observation techniques enable us to elucidate the transport properties of unoccupied states on solid surfaces. Among them, image-potential states (IPSs) are of particular importance, since they appear ubiquitously on metal surfaces, exhibiting a Rydberg series with parabolic dispersions. From an applicational point of view, IPSs could influence the properties of molecular-based electronic devices such as organic light-emitting diodes, interacting with unoccupied molecular orbitals of adsorbates. Recently, we have applied van der Waals density functional (vdW-DF) method [1] to naphthalene physisorbed on graphene and revealed that IPSs are induced on close-packed naphthalene monolayer, hybridizing with graphene IPSs [2]. The resultant hybrid IPSs show an anisotropic effective mass that reflects the molecular structure of naphthalene, demonstrating that the transport properties of IPSs of metal surfaces can be fine-tuned by molecular adsorption.

As an extension of our previous study on hybrid IPSs at molecular-metal interfaces, we here theoretically investigate lead phthalocyanine (PbPc) physisorbed on graphene



Fig. 1: Determination of the equilibrium distance between PbPc and graphene

as shown in Fig. 1. Experimentally, IPSs of PbPc adsorbed on HOPG has been investigated intensively using two-electron photoemission spectroscopy [3-5]. Unlike naphthalene, PbPc has a non-planar shuttlecock structure due to the central lead atom, which results in a dipole moment. To understand the influence of the dipole moment on hybrid IPSs, we investigate the band structure of PbPc on graphene and analyze the effective mass of the IPSs. Our results reveal that the dipole moment reduces the overlap of wave functions between neighboring molecules, which enhances the effective mass of the hybrid IPSs. Moreover, unlike the IPSs of graphene, the hybrid IPSs in PbPc on graphene displays an anisotropic effective mass with

nearly C₄ symmetry, which prominently reflects the molecular structure of PbPc [6].

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STM simulations for Fe-adsorbed Si(111) surfaces

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Using scanning tunneling microscopy (STM), author's group has been studied iron-silicides formation on Si(111) [1] prepared in ultra-high vacuum. In the initial stage of Si(111)7×7 with isolated Fe atoms, we observed 5 different adsorption types in experimental STM images [2]. In order to understand (meta) stable actual structures of Fe/Si(111)7×7, we carried out first principles calculations using the super computing system in the institute for solid state physics.

We utilized the calculation package of Simulation Tool for Atom TEchnology (STATE)-Senri [3] for 17 models of Fe single-atom adsorption including *atop*, *ins*, T_4 , and H_3 sites, based on a Si(111)4×4 surface-substrate model [4]. The 4×4 model (i.e., 4 Si adatoms on 2×2 T_4 sites, and 2 of 4 restatoms terminated with H atom, in a unit) has an advantage of fast calculation, because of smaller number of atoms compaired to that in the 7×7 model, maintaining the specific Si surface property of the 7×7 model of the dimer–adatom–stackingfault, though the 4×4 model is not equal to the 7×7 model.



Figure 1: A model of $Si(111)4 \times 4$ clean surface and STM simulation results.

The clean Si(111)4×4 model consisting of a Si adatom-layer, six Si-layers, and a bottom H-terminated layer has 118 atoms, while 7×7 has 347 atoms. The top-view and side-view schematics in Fig. 1 show the atomic structure of the clean 4×4 model; upper adatom (brawn ball) corresponds to center adatom (CEA) with two neighbored restatoms (purple ball, note another restatom is terminated by H atom), and lower adatom corresponds to corner adatom (COA). The bottom panel represents STM simulation images of filled (empty) states at -0.5 (+0.5) V in bias voltage, displaying clear adatom images.

In the simulation, the atoms in the top six layers were relaxed with the spin polarization, from the converged configurations without the spin polarization.



Figure 2: A model of $Si(111)4 \times 4$ surface with Fe atom near a H₃ site and STM simulation results.

During the 17 models, the stable configuration was Fe atom close to H_3 site as shown in Fig. 2; Fe atom (pink ball) locates between CEA and restatom, with the formation energy of -7.59 eV. The STM images showed darken adatom at filled states at -0.5 V while no drastic change at empty states at +0.5 V. The second (meta) stable configuration was also near H_3 site COA and restatom with the formation energy of -7.55 eV. The third meta-stable configuration group was near T_4 sites with -6.87 eV to -6.35 eV in formation energy. The fourth group was *ins* sites with -6.34 eV to -6.28 eV, and the last (much unstable) group was *atop* sites with -5.32 eV to -5.28 eV.

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Analysis on atomic and magnetic structure in magnetic molecular complex, crystal and interface and investigation of external field effect

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We have investigated the weak-bound magnetic material systems such as magnetic molecular crystal and magnetic-layered material. They have received a lot of attention due to their unique physical properties, such as external field-controllable its magnetization and crystal structure. Since prediction of structural and energic properties with high accuracy is essential for weak-bond magnetic materials, we have enhanced the computational accuracy of density functional theory (DFT) by including physical interactions, e.g. van der Waals (vdW) interaction and magnetic dipole-dipole (MDI) energy, which were neglected in standard DFT calculation. While MDI energy is often considered as weak, it plays important role for magnetic anisotropy (MA) and diamagnetic field. Moreover, we also attempt to build a framework to investigate the external magnetic field effect.

We developed the method for each material dimensionality (chain, film, bulk) to estimate their MDI energy, since MDI interaction is basically long-range interaction proportional to minus cube of distance. It can be estimated using spatial spin density obtained from DFT calculation. We applied this approach to antiferromagnetic molecular crystal [1] (monoclinic crystal solid oxygen α phase: α -O₂) and ferromagnetic thin film and chain (Fe, Co, Ni). We found that its contribution to MA is comparable to those of Spin-Orbit Interaction. Moreover, the spatial distribution of intra-atomic spin density occasionally contributes to MDI energy. For solid oxygen α phase case, noncolinear spin-dependent vdW-DF method, which developed in our previous work [2], was employed. External magnetic field effect due to Zeeman interaction can be considered for oxygen α -phase case, in order to investigate the effect towards its magnetization [3].

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Effects of electron-phonon scattering on electronic structure of half-metallic Heusler alloys

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In some Heusler alloys, despite the fact that there exists a band gap in one of spin channels expected, established through first-principles calculations, the half-metallicity of the materials often turns out fragile under realistic situations such as in device structures. It has been pointed out that chemical disorders and defects might easily degrade the half-metallic nature of such materials. These degradations are structure oriented, and therefore, static. This means, once a perfect structure is attained, there exists no reason of this kind of degradation for the half-metallicity. However, there still exist another source of degradation, i.e., dynamical effects. The main sources of such effects are phonons and magnons at finite temperature. In the present research, we discuss the effects of electron-phonon scattering on the half-metallicity of Co₂MnSi, as a typical example, on the basis of first-principles calculations. The phonons are treated as giving local and static (adiabatic) effects [1], where correlations of the displacements between neighboring sites as well as dynamical effects are neglected, i.e. we take a quasi-dynamical treatment. The phonons are expressed as random displacements of atoms from their equilibrium positions. Using the distribution of the atomic displacements, the electronic structures of the system at finite temperature are calculated by regarding the system as a disordered system with randomly distributed atomic positions. This kind of randomness can be treated using KKR-CPA code [2]. The results show

that even at 300 K, the perfect half-metallicity is lost (Fig.1), showing that the effects of phonons are important at usual operating temperatures of devices. The effects on the GMR is also discussed. It turns out that, though the half-metallicity is lost at finite temperature, the conductivity of the spin-down state is much lower than that of the spin-up state by virtue of the strong electron-phonon scattering. Thus, the system can still be used in GMR devices at finite temperatures.



Figure 1: DOS of Co₂MnSi with an average displacement $\langle u^2 \rangle = 0$ (left) and 0.046 (right) in units of Bohr².

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Systematics of Curie temperature in rare earth permanent magnet materials

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Curie temperatures $T_{\rm C}$'s of permanentmagnet materials $R_2(\text{Fe},\text{Co})_{14}\text{B}$, $R_2(\text{Fe},\text{Co})_{17}$, and $RFe_{11.5}Ti_{0.5}$ (R = La, Ce, ..., Lu, Y), are calculated within the mean field approximation using the exchange coupling constants J_{ij} 's that are obtained by first-principles KKR–Green's function method[1]. While the agreement between the calculations and experiments is rather well for the Co-based systems, there arise some discrepancies in the case of Fe-bases systems. Despite these discrepancies, however, the systematic changes seen in $T_{\rm C}$ as the rare earth element R changes across the lantanoid are fairly well reproduced by the calculation. In the case of R_2 Fe₁₄B, the discrepancies can be largely diminished by using J_{ij} 's that are calculated for local-moment disordered states (LMD), which is considered to correspond to the paramagnetic state above $T_{\rm C}$, as is shown in Fig.1 and 2. However, this is not the case in general: the discrepancies seen in R_2 Fe₁₇ (FIg. 3), cannot be remedied. From the analyses of calculated and experimental data, it is concluded that data assimilations are possible and necessary to make reasonable predictions of $T_{\rm C}$ for rare earth permanentmagnet materials, in particular, the Fe-based ones.

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Figure 1: Calculated $T_{\rm C}$ of R_2 Fe₁₄B compared with experiments.



Figure 2: Calculated $T_{\rm C}$ of $R_2 {\rm Co}_{14} {\rm B}$ compared with experiments.



Figure 3: Calculated $T_{\rm C}$ of $R_2 \text{Fe}_{17}$ compared with experiments.

Electronic state of water under various environments

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We have studied aqueous solution using massive parallel computer simulations. This year, we focus on aqueous oxalic and malonic acid observed by X-ray absorption and emission spectroscopy [1]. To obtain the theoretical spectra of an aqueous solution, a molecular dynamics (MD) simulation based density functional theory (DFT) was adopted to simulate the structure of the solution. The MD simulations ware performed using the Vienna ab initio simulation package (VASP). The MD simulations ware performed for 5 ps, with 0.2fs time steps. Cluster sampling was performed using python and fortran code for the results of the MD simulations. From the cluster obtained by structure sampling, a carboxylic acid molecule at the center of the cluster was used to model the OC=O,1s and OC-O-,1s core-hole and core excited state dynamics. The time steps used for these simulations were 0.25 and 20 fs, respectively. During the core excited state dynamics, each snapshot was used to calculate the relative line intensities of the X-ray



Fig. 1: (a) XAS and (b) XES spectra of aqueous oxalic acid (solid line: experiment, dash: theoretical, black: pH 1.1, red: pH 2.7, green: pH12.9).

emission spectra. The core excited dynamics and relative peak intensities of the spectra were calculated within the framework of DFT using deMon2k code.

We found that the theoretical XAS and XES spectra of cluster models reproduced the trends of the experimental spectra with respect to emission energy compared with single molecular models. We found that the dependence of XAS and XES spectra on pH is different from monocarboxylic acid.

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Temperature-Dependent Optical Properties in Rare-earth Sesquioxides and Related Phonon Calculations

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The natural oxide of Si, amorphous SiO₂, is important for the CMOS technology. Due to the problem related to its fundamental size limits, reduction of the gate-oxide thickness in devices is strongly demanded. As one of the expected candidates satisfying these properties, attention is paid on rare-earth metal sesquioxides. Their optical properties are almost far from the full understanding. It is expected that such a temperature-dependent optical study can yield in several insights not only on electronic or excitonic properties, but also on phononic properties. In this activity report, we report the optical properties and related phonon calculations of ytterbia (Yb₂O₃) and lutetia (Lu_2O_3) thin films.

The phonon properties of the structure are obtained by a frozen phonon method: The forces acting on the ions are calculated upon a small displacement of each ion by using Quantum ESPRESSO package. The set of forces can be converted into the force constants, which are required to construct the dynamical matrix. We used the PHONOPY package to generate a set of $2 \times 2 \times 2$ supercells with displaced atoms, to compute the phonon dispersion and density-of-states (DOS) spectra. Figure 1 shows temperature dependences of the band-gap energies. Alloted symbols are open circles for ytterbia and open squares in lutetia, respectively. We here use Pässler model to fit to the experimental data. the detailed values of deduced parameters have been given elsewhere [1]. We could reduce of the number of running parameters in the regression analysis which are an advantage and significance of the abovementioned phonon-property-related discussion.

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Fig. 1: Temperature dependences of band-gap E_g in Yb₂O₃ (circles) and Lu₂O₃ (squares).

First-principles calculation of organic modified metal oxide nanoparticles

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We have studied an interface system of organic molecules on metal oxide surface. From the experiments, it is known that surface stability of metal oxide greatly changes depending on the environment, resulting in the difference in the properties. For example, CeO₂ is ordinary stable with (111) surface, but it turns to be stable with (100) facet when hydrothermally treated with carboxylic acid. As a result, catalytic activity is greatly enhanced with (100) facet exposure of CeO₂ [1]. In this year, we studied the interaction between octanoic acid and CeO₂ surface using firstprinciples simulation.

Plane-wave basis density functional theory simulations were conducted with VASP code. Simulations were The generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE) represented the exchangecorrelation energy functional. The DFT+Umethod introduced by Dudarev was used to treat electron localization. The parameter U-Jwas set to 5.0 eV for Ce4f state. The valence configurations of the pseudopotentials were $5s^25p^64f^15d^16s^2$ for Ce, $2s^22p^4$ for O, and $2s^22p^2$ for C. The energy cutoff for the plane-wave basis was set at 500 eV for all the calculations. Monkhorst-Pack k-point set of $4 \times 4 \times 1$ was used for the a slab model. Convergence criteria was set at less than 0.01 eV/Å for the force.

Figure 1 shows the adsorption, deprotonation, and dehydration of octanoic acid on CeO₂ (100) surface considered in this study. From the results, energy stabilization was calculated as -26.63 kJ/mol for adsorption and -26.57 kJ/mol for deprotonation. Deprotonation does not contribute stabilization. Dehydration of octanoic acid and hydroxide on CeO₂ surface, much larger stabilization as -43.20 kJ/mol was observed.



Figure 1 Adsorption, deprotonation, and dehydration of octanoic acid on CeO₂ (100)

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First principles study on leaking current at a dislocation in doped semiconductors

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In the second half fiscal year of 2019, we have revealed the following results related with the performance of gallium nitride (GaN) power devices [1].

• The threading screw dislocations attract Mg impurities, and the electronic levels in the energy gap induced by the threading dislocations elevate towards the conduction band as the Mg approaches the dislocation line.

This results suggest that the leakage current which degrade the performance of the devices is induced by the presence of the Mg and the screw dislocation complexes.

GaN is one of the most promising compounds for the power devices since it has a large band gap. For the realization of the device, suppressing the leakage current is an important issue. The leakage current has been observed at the position of the threading dislocation. Recent experimental study suggests that the Mg impurities are condensed around the dislocation. The electronic structure of the Mg-dislocation complexes should be related with the origin of the leakage current, and it is important to guarantee the device reliability.

In this study, we systematically perform first-principles total-energy calculations for possible 16 core structures of the screw dislocations as shown in Fig. 1. The core structures are expressed as $D(n \mid m)$ or $S(n \mid m)$. The first capital letter denotes the position of the dislocation line. One is called single core,



Figure 1: The 16 core types of the screw dislocations. A red cross in the top panel denotes the position of the dislocation line. The left is for $D(n \mid m)$ and the right is for $S(n \mid m)$, where n is the number of removed Ga and m is that of N.

in which the dislocation line is at the center of the single hexagon; Another is called double core, in which the dislocation line is at the middle of the bond of hexagon. n and m represent the numbers of Ga and N atoms removed from the fully filled structures. An example of $D(0 \mid 0)$ is shown in Fig. 2

Those first-principles calculations are done by using the Vienna Ab initio Simulation Package (VASP) [2] which is based on the projector augmented-wave (PAW) method. The exchange-correlation energy is treated within the generalized gradient approxima-



Figure 2: The core structure $D(0 \mid 0)$. Green and blue spheres denote Ga and N, respectively. The atoms surrounding the dislocation line are enlarged to emphasize the position.

tion (GGA) with the Perdew-Burke-Ernzerhof functional. We also use the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional to evaluate more accurate electronic levels in the band gap. The unit cell contains about 800 Ga and N atoms in total. The GaN pillar is surrounded by the vacuum on the lateral directions perpendicular to the [0001]. We expect that this vacuum relaxes artificial strain caused by rounding the lateral surfaces. The dangling bonds on the lateral surface of the GaN pillar are terminated by ≈ 100 fictitious hydrogens. The schematic picture of the unit cell on the [0001] plane is shown in Fig. 3. The integration over Brillouin zone is taken with 4 sampling points along the [0001] direction. The structural optimization is performed for each core structures.

We found that D(0 | 2), S(0 | 3), and S(0 | 6)are stable. Then we replace one Ga atom in these three core structures with an Mg atom. The relative position of the Mg from the dislocation line is sampled. The resultant binding energy of the Mg shows that Mg is attracted by the screw dislocation and the electronic levels in the gap elevate towards the conduction band, as mentioned above.



Figure 3: A schematic picture of the [0001] plane of the unit cell. The green region denotes GaN and it is terminated by the fictitious hydrogen atoms. The outermost region is the vacuum. A red cross denotes the position of the dislocation line.

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Ab Initio Band Structure Calculation of InSb Using VASP Based on Hybrid Density Functional Theory

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Terahertz-wave frequency range (0.1 to 10 THz) will be the major resources in future communication and sensing systems. InSb channel high electron mobility transistors (HEMTs) are one of the most promising devices that can operate in the terahertz band. Although InSb has the lightest electron effective mass in III-V semiconductors, the lattice constant of InSb is the largest. Therefore, compressive strain is always applied to the InSb channel.

In our previous work [1], we carried out Monte Carlo (MC) simulations of InSb channel HEMTs to predict device performance. We used the band parameters calculated by the empirical pseudopotential method [2]. However, the band structure obtained from the first-principles calculation seems to be preferable. In 2018, we carried out ab initio band structure calculations of unstrained and compressively strained InSb using Vienna Ab initio Simulation Package (VASP) based on the method in the local density approximation to obtain band parameters [3]. We obtained nonzero bandgap energy E_g values by using PBE0 (Perdew-Burke-Ernzerhof 0) as a functional. In this work, we investigated functionals used for band structure calculation in order to obtain the E_g values close to the literature ones.

We studied the hybrid coefficient of the density functional [4]. The hybrid functional used in this work was a modification of PBE0. The functional is constructed by the mixing of a fraction α of the Fock exchange with a fraction $1 - \alpha$ of the PBE exchange. The exchange-correlation energy E_{xc} can be expressed by the following equation:



Fig. 1 Calculated bandgap energy as a function of mixing coefficient, α .

$$E_{xc} = \alpha E_x + (1 - \alpha) E_x^{PBE} + E_c^{PBE}$$
(1)

where E_x is the Fock exchange, E_x^{PBE} is the PBE exchange, and E_c^{PBE} is the PBE correlation [4]. In PBE0, the mixing coefficient $\alpha = 0.25$. In our previous work [3], we obtained the bandgap energy E_g values of unstrained and compressively strained InSb. However, the E_g values are too large when using $\alpha = 0.25$ (PBE0). We calculated the bandgap energy values as a function of α . Figure 1 shows the calculation results of bandgap energy. We obtained the closest bandgap energy E_g to the previous work [5, 6] with $\alpha = 0.21$.

Table 1 summarizes the band parameters of InSb in Refs. [3, 5, 6] and in this work. In our previous work [3], we obtained the bandgap energy E_g of 0.34 and 0.48 eV for unstrained (0%) and compressively strained (-1.32%) InSb, respectively. The E_g value for unstrained InSb in [3] is much larger than that in [5, 6]. In the present work, the E_g value was relatively reasonable because the mixing coefficient α was set to match the "general" bandgap value of InSb [5, 6]. On the other hand, the increase in E_g when compressive strain is applied seems to be small for $\alpha = 0.21$. The electron effective mass in the Γ valley m_{Γ}^* of unstrained InSb is almost same as the values in the previous results [3, 5, 6]. However, the increase in the value of m_{Γ}^* for the -1.32% compressively strained InSb also appears to be small. Furthermore, there is room for reconsideration of the energy difference between Γ and L valleys, $E_{\Gamma-L}$ and Γ and X valleys, $E_{\Gamma-X}$.

Regarding the mixing coefficient of the density functional, further work is necessary considering the correspondence with various literature and experimental values.

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	0%	0%	-1.32%	0%	-1.32%
	[5, 6]	(VASP)	(VASP)	(VASP)	(VASP)
		[3]	[3]	[This work]	[This work]
$E_q(eV)$	0.18	0.34	0.48	0.151	0.154
m_{Γ}^{*}	0.014	0.015	0.022	0.012	0.013
$E_{\Gamma-I}$ (eV)	0.76	1.04	1.06	1.05	1.05
$E_{\Gamma-X}(eV)$	0.46	2.64	2.69	2.64	2.64

Table 1 Main band parameters of InSb.

First-principles investigation of electronic properties of carbon nanotubes and graphene

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Graphene and carbon nanotubes (CNTs) show high charge mobility at room temperature, and therefore they are expected to be a promising device material to be used in nanoelectronics such as field-effect transistors. Substitutional doping is one of the effective ways to tune the electronic properties of graphene and CNTs, and is also shown to improve the chemical reactivity to adsorbates. Therefore dope graphene and doped CNTs are a good candidate for future sensor device materials.

We here present the adsorption properties of toxic NO and NO₂ molecules on the borondoped graphene and (8,0) CNT using a firstprinciples density-functional calculation [1, 2, 3]. It is found that the NO and NO₂ molecules can be adsorbed strongly with short distances and large adsorption energies on the B-doped monolayer graphene [2]. For the AB-stacked bilayer graphene, NO and NO₂ molecules can be also strongly adsorbed [1, 3]. It is also found that the adsorption energies of NO and NO₂ molecules on the B-doped (8,0) CNTs are much larger than those of monolayer and bilayer graphenes.

Table 1 lists the adsorption energies and the

Table 1: Adsorption energy E_a (eV) and distance d (Å) between adsorbed molecule and B atom for molecules adsorbed on B-doped monolayer and AB-stacked bilayer graphenes.

	Monolayer	Bilayer		
	E_a	d	E_a	d
NO	-1.23	2.15	-1.19	2.14
NO_2	-1.16	1.59	-1.13	1.60

distances between the B atom in the doped graphene layer and the adsorbed molecules for NO and NO₂ molecules on the B-doped monolayer and AB-stacked bilayer graphenes. The NO and NO₂ molecules are found to be adsorbed strongly with short distances and large adsorption energies on the B-doped monolayer graphene. For the case of the AB-stacked bilayer graphene, it is interesting that the adsorption energies as well as the binding distances for the adsorptions of the NO and NO₂ molecules are comparable to those of the Bdoped monolayer graphene.

We also study the adsorption energies and the binding distances of NO and NO₂ molecules on the B-doped (8,0) carbon nanotubes (CNTs). Like monolayer and bilayer graphenes, the NO and NO₂ molecules are found to strongly bind on the B-doped (8,0) CNTs with the large adsorption energies and the short binding distances. Furthermore, the adsorption energies for NO and NO₂ molecules on the B-doped (8,0) CNTs are considerably larger than those on the Bdoped monolayer as well as the B-doped bilayer graphenes due to the curvature effects.

In summary, we have studied the adsorption properties of the toxic NO and NO₂ molecules on the B-doped graphene and Bdoped (8,0) CNT, based on first-principles density-functional calculations. The NO and NO₂ molecules strongly bind on the B-doped monolayer and bilayer graphenes. The adsorption energies of NO and NO₂ molecules on the B-doped (8,0) CNTs are larger than those on the B-doped graphene layers.

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Study of appearance of ferromagnetism by electric field application to Pt thin film

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Recently, It was reported that ferromagnetism appears in an oscillatory manner in the Pt(100) thin films depending on the film thickness[1][2]. This property suggests that magnetism in Pt(100) thin film can be controlled by electric field. In order to clarify the magnetism change with application of electric field, we performed first-principles calculation using the PHASE/ 0 program.

The first-principles calculation based on the DFT within the GGA was performed, where Vanderbilt type pseudopotential and a planewave basis set were used to evaluate electric structure and magnetization of Pt(100) thin film. We used $88 \times 88 \times 1$ k points (based on Monkhorst-Pack) and a cutoff energy of 36 Rydberg.

We calculated lattice constant that minimizes the energy. Using the obtained lattice constant, we calculated the Pt layer thickness dependence of the magnetic moment of Pt slab. Calculations of electronic structure for the free-standing Pt(100) thin films from 2 monolayers(ML) up to 17 ML were performed and it was clarified that the ferromagnetism appeared in oscillatory manner with a period of 6 ML only when spin-orbit interaction (SOI) was not included (Fig.1). This oscillatory behavior agrees with the experiment[2]. These results suggest that magnetism in Pt(100) thin film is intrinsically unrelated to SOI. For the next step, we calculate magnetism in Pt(100) thin film under application of electric field.



Fig. 1: Thickness-dependent magnetic moment per Pt atom.

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Ab Initio Calculation of High-Rate Deposition of Copper Film by Low-Pressure Chemical Vapor Deposition with CuI on Ru Substrate

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We have studied low-pressure chemical vapor deposition of Cu on Ru substrate using CuI [1] using VASP program package (MPI parallelization with multiple threads). This year, we focused on the molecular mechanism of adsorption, migration and desorption. This is a collaborative work with the experimentalist [2] (Prof. Satoshi Yamauchi at Ibaraki University), who conducted the LPCVD experiment.

In this study, we elucidated the molecular mechanism of Cu deposition using copper(I) iodide (CuI) on Ru substrate by low-pressure chemical vapor deposition through electronic structure calculations. Using density functional theory calculations, we show that CuI molecules adsorb and decompose exothermically due to a strong adsorption of iodine atoms onto the Ru(001) surface. The rate-limiting step of the Cu deposition is found to be the desorption of iodine molecules from the Cu(111) surface, suggesting that the removal of iodine species is necessary to achieve the high-rate deposition of highlyconductive copper films for ultra large scale

integration metallization.

Based on this study, we are now extending our calculations to analyze the dynamical properties in more detail. In addition, new sets of precursor and substrate are explored for ultra large scale integration metallization together with experiment.



Fig. 1: Molecular mechanism of LPCVD of Cu.

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Theoretical Analysis of Photocatalytic Reaction Mechanism at Titanium Dioxide Interfaces

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We have studied photocatalytic reaction mechanism at anatase TiO₂ surfaces [1] using cp2k program package (MPI parallelization with multiple threads). This year, we focused on the energetics and structure during the hole migration. This is a collaborative work with the experimentalist [2] (Prof. Satoshi Yamauchi at Ibaraki University), who conducted the LPCVD experiment.

Anatase TiO₂ shows a high photocatalytic activity to decompose organic compounds and plays a crucial role in chemistry and physics. To enhance the photocatalytic activity, proper control of surface properties is crucial and the molecular-level mechanism can offer valuable insight. We herein clarify the facet dependence of hole trapping at the anatase TiO₂ surface by density functional theory (DFT) calculations using the constrained DFT method with the hybrid functionals. The photocatalytic activity by UV irradiation around 365 nm in methylene blue aqueous solution is significantly high, which is two-order larger than that on the multi-oriented TiO₂. The DFT calculations show the (112) surface can stabilize water adsorption and the photogenerated hole can be trapped not on the neat surface but on the hydroxylated surface better at the (112) and (001) surfaces. The experimental and theoretical findings elucidate that the (112) facet shows the larger stabilization of absorbed water and trapped holes than other facets by larger structural relaxation at the surface.





Fig. 1: Molecular mechanism of hole migration.

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Search and realization of novel electronic properties of solid surfaces and interfaces and of small particles

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We mention two subjects which we addressed this year.

Graphene is a very popular single-layer structure of carbon (C) atoms arranged in a hexagonal lattice. However, we explore different monolayer structures of C atoms. Previously, we showed that the monolayer structure in Fig. 1 is stable, and that the electron system is a semi-metal which is characterized by the electron pocket around the \overline{M} point and the hole pocket around the $\overline{\Gamma}$ point. We applied the tight-binding method to this system and clarified its utility and limitation for this system.

In scanning tunneling microscopy (STM) light emission spectra of Ni(110)–(2x1)–O surface emerge stepwise structures due to oxygen (O) atom vibration parallel to the surface [1]. These structures are considered to arise from the change in the local density of states (LDOS) below the STM tip owing to the vibration [1]. Using first-principles calculations, we examined the variation in LDOS due to adiabatic in-plane displacement of an adsorbed O atom.

We employed the program package 'Vienna Ab initio Simulation Package' (VASP) [2,3] on systems B and C.

(1) Application of the tight-binding method to a novel single-layer structure of carbon atoms [4]

The above-stated electron pocket and hole pocket are formed the bv π -orbital-derived bands around the Fermi level $E_{\rm F}$. Therefore, we can expect that the tight-binding method in terms of p_z orbitals of C atoms is effective for this system. Figure 2 exhibits the band dispersion on the $\overline{\Gamma}$ – \overline{M} line for the hybrid density -functional method (Hyb) and the tightbinding method (TB). The transfer integral for a diagonal nearest-neighbor p_2 pair and that for a lateral nearest-neighbor p_z pair were chosen to be -2.9 eV and -3.2 eV, respectively. In view of band dispersions on other symmetric dispersion lines as well, we found that the tight-binding method can reproduce adequately the band dispersions around $E_{\rm F}$, and consequently the electron and hole pockets. The tight-binding method provides a useful tool for evaluating electronic properties of this system arising from π -orbital-derived bands.



Fig. 1 Carbon monolayer structure considered here



Fig. 2 Band dispersions on the $\overline{\Gamma} - \overline{M}$ line for the hybrid density -functional method (Hyb) and the tight- binding method (TB).

(2) Electronic structure of Ni(110)–(2x1) O surface [5]

Last year, by means of the generalized gradient approximation, we investigated the ground state of a proposed promising namely, the missing-row structure. reconstructed O p(2x1)/Ni(110) surface. We optimized a slab composed of 11 Ni atom layers and an O atom adsorbed at each surface. This year, for a 21 Ni atom -layer slab, we treated phonon vibration adiabatically, and examined the change in the orbital-projected DOS (op-DOS) at each atom when O atoms are displaced in the surface-parallel direction. We optimized the structure when the distance between the O atom and the Ni atom numbered 40 (see Fig. 3) in the y direction is reduced by a certain length and fixed. The height of the O atom measured from the No.40 Ni atom is 0.29 Å in the ground state. As the O atom gets closer to the No.40 Ni atom by 0.3 Å, this height rises to 0.71 Å. We pay attention to p orbitals of the O atom and d orbitals of Ni atoms. We analyzed the variation in the op-DOS at each atom due to O-atom displacement. Here, we present a part of our results for majority spin originating from ferromagnetic Ni. Figure 4 exhibits the p_{ν} -projected DOS at the O atom which is quite important in the STM experiment with the tip placed right above the O atom. The broken curve marked 'GS' and the full curve labelled as '0.3 Å disp' display the results for the ground state and for 0.3Å displacement in the y direction, respectively. The peak around the Fermi level $E_{\rm F}$ shifts to the higher energy side, and the peak intensity increases with O-atom displacement. The peak position reaches $E_{\rm F}$ at 0.3 Å displacement. The peak in the p_v -projected DOS for minority spin also shows a similar shift to the higher energy side. Our analysis including d-orbital-projected DOS at Ni atoms indicated that approach of the O atom to the No.40 Ni atom leads to stronger hybridization between the p_{γ} orbital of the O atom and the d_{yz} orbital of the Ni atom. The above peak shift implies that the phonon vibration affects the STM light emission through the change in opDOS.



Fig. 3 Optimized slab structure of O p(2x1) Ni(110) surface. The slab is composed of 21 Ni atom layers and an adsorbed O atom at each surface.



Fig. 4 p_y -orbital-projected density of states at the adsorbed O atom for the ground state and for O-atom displacement by 0.3 Å.

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Atomic and electronic structures of intermetallic compound catalysts

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In this fiscal year we have studied the initial stage of oxidation of $Ni_3Al(210)$ and PdZn(111) surfaces. All calculations are caried out using VASP with the PAW method and the PBE exchange-correlation functional.

It was reported that Ni₃Al is highly active for hydrogen production from methanol and methane, and its catalytic performance is considered to be attributed to the selective oxidation and hydroxylation of Al and the formation of metallic Ni particles at low oxygen partial pressures[1]. An X-ray photoelectron spectroscopy study shows Al oxide is formed preferentially in the beginning of the oxidation process, and Ni oxides start to form at 1.6 ML oxygen coverage[2]. We first searched for the stable adsorption sites at 0.25 and 0.5ML. In both cases, it turned out that the most stable adsorption site is a pseud-threefold site surrounded by two Al atom at the top layer and one Ni atom at the second layer. The adsorption geometry is similar to the result reported for NiAl(110)[3], but this structure is not consistent with the XPS experiment showing no sign of Ni oxides formation at this coverage. Inspired by the previous study[3], we introduced some antisite defects in the oxidized surface, and it is found that antisite defect stabilizes the surface when they form a specific structure. According to the simulated STM images using the Tersoff-Hamann approximation, this structure shows a unique image easily distinguished from other structures with different antisite arrangement or without the defect.

Although pure Pd is not active for methanol steam reforming (MSR), PdZn exhibits comparable catalytic activity and selectivity to the conventional Cu catalyst in MSR. Recently, some groups reported that ZnO formed during the reaction is essential for the catalytic performance of PdZn. However, this is not straightforward because Zn has no d-state around the Fermi level implying the chemical inactivity of ZnO. We first determined the stable adsorption structure of oxygen on PdZn(111), and investigated the electronic structure of this system. We previously reported that bulk PdZn has a similar electronic structure to Cu[5], but the Pd 4d-band of PdZn is broadened when oxygen is adsorbed. It was also found that Zn-d states appear below the Fermi level when oxygen adsorbs on the most stable site.

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Switching of magnetism via modifying phase shift of quantum-well states by tailoring the interface electronic structure

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In this project, we expanded Phase model for the Quantum-well states (QWs), and suggested the method to control the QW induced ferromagnetism in Pd(100) by changing scattering phase shift. Then, we verified this theory using density functional theoretical (DFT) calculation [1].

The following Phase model, describing the QWs, indicates the conditions under which a standing wave can exist:

$$2k_z d + \Phi = 2\pi n,\tag{1}$$

where k_z is the confined wave number, d is the film thickness, Φ is the scattering phase shift at surface and interface, and n is an integer quantum number. Previous experiments and DFT calculations showed that the period of oscillation by modification of magnetic properties via QWs is expressed as $p = 1/k_{Fz}$, where pis the period of oscillation (where thickness of the film is d) and k_{Fz} is the vertical Fermi wave number i.e. the Fermi wave number of the confined band. This and eq. (1) indicate that the confined wave number k_z reaches Fermi energy periodically depending on the film thickness dand the phase shift Φ is unrelated to the period of oscillation.

Previous DFT calculations and experiments predicted that $d_{xz,yz}$ electrons are confined at the QWs of Pd(100) films, and this induces ferromagnetism in Pd(100) ultrathin films. These orbital characters express one dimensional dispersion in the in-plane direction. For these electrons, phase shift Φ of the QWs might depend on k_x, k_y , and ϵ . Thus, it is necessary to expand the phase model to include k_x and k_y (i.e. the wave number of the in-plane direction \mathbf{k}_{\parallel}) dependencies.

First, $k_z(n) = (2\pi n - \Phi)/2d$ is defined from eq. (1). Then, the *n*-th energy level of Pd(100) film quantum well $\epsilon_{\text{QW}}(n, \mathbf{k}_{\parallel})$ can be obtained from the Pd bulk energy band structure $\epsilon(k_z, \mathbf{k}_{\parallel})$ as

$$\epsilon_{\text{QW}}\left(n, \boldsymbol{k}_{\parallel}\right) = \epsilon\left(k_{z}(n), \boldsymbol{k}_{\parallel}\right),$$
 (2)

where $\mathbf{k}_{\parallel} = (k_x, k_y)$ is the in-plane wave vector because the band dispersion of the QWs is a projection of the specific bulk band. Then, the binding energy of the quantum-well state $\epsilon_{\rm QW}$ in Pd(100) can be described by expanding $\epsilon_{\rm QW}$ around the Fermi energy as

$$\epsilon_{\rm QW}\left(n, \boldsymbol{k}_{\parallel}\right) \sim \epsilon_{\rm F} + \left[k_{z}(n) - k_{\rm Fz}\right] \frac{\partial \epsilon}{\partial k_{z}} \left(k_{\rm Fz}, \boldsymbol{k}_{\rm F\parallel}\right) + \Delta \boldsymbol{k}_{\parallel} \cdot \frac{\partial \epsilon}{\partial \boldsymbol{k}_{\parallel}} \left(k_{\rm Fz}, \boldsymbol{k}_{\rm F\parallel}\right),$$
(3)

where $\mathbf{k}_{\mathrm{F}\parallel}$ is the in-plane Fermi wave vector, $\Delta \mathbf{k}_{\parallel} = \mathbf{k}_{\parallel} - \mathbf{k}_{\mathrm{F}\parallel}$, and $\epsilon_{\mathrm{F}} = \epsilon \left(k_{\mathrm{F}z}, \mathbf{k}_{\mathrm{F}\parallel} \right)$.

Considering Pd bulk band dispersion, dispersion of $d_{xz,yz}$ has a flat shape around Γ point and zone edges. Therefore, in Pd(100) film, the following relation is satisfied:

$$\frac{\partial \epsilon}{\partial \boldsymbol{k}_{\parallel}} \left(k_{\mathrm{F}z}, \boldsymbol{k}_{\mathrm{F}\parallel} \right) \sim 0. \tag{4}$$

According to eq. (5), this means that $\epsilon_{\text{QW}}(n, \mathbf{k}_{\parallel})$ almost coincides with the Fermi energy ϵ_{F} being independent of \mathbf{k}_{\parallel} , if $k_z(n)$ matches $k_{\text{F}z}$. Then the density of states at the Fermi energy $D(\epsilon_{\text{F}})$ diverges and induces ferromagnetism from the standpoint of the Stoner criterion. The condition $k_z(n) = k_{\text{F}z}$ leads to oscillatory appearance of ferromagnetism with the periodicity p depending on the film thickness d.

Now we extend the theory above as shall be discussed later, the phase shift Φ generally depends on \mathbf{k}_{\parallel} . If we permit such \mathbf{k}_{\parallel} dependence for Φ , $k_z(n)$ also depends on \mathbf{k}_{\parallel} . Since $k_z(n, \mathbf{k}_{\parallel}) = (2\pi n - \Phi(\mathbf{k}_{\parallel}))/2d$ eq. (5) must be modified into

$$\begin{aligned} \epsilon_{\rm QW} \left(n, \boldsymbol{k}_{\parallel} \right) &\sim \epsilon_{\rm F} \\ &+ \left[k_z(n, \boldsymbol{k}_{\rm F\parallel}) - k_{\rm Fz} \right] \frac{\partial \epsilon}{\partial k_z} \left(k_{\rm Fz}, \boldsymbol{k}_{\rm F\parallel} \right) \\ &+ \Delta \boldsymbol{k}_{\parallel} \cdot \frac{\partial \epsilon}{\partial \boldsymbol{k}_{\parallel}} \left(k_{\rm Fz}, \boldsymbol{k}_{\rm F\parallel} \right) \\ &+ \Delta \boldsymbol{k}_{\parallel} \cdot \frac{\partial k_z}{\partial \boldsymbol{k}_{\parallel}} (n, \boldsymbol{k}_{\rm F\parallel}) \frac{\partial \epsilon}{\partial k_z} \left(k_{\rm Fz}, \boldsymbol{k}_{\rm F\parallel} \right), \end{aligned} \tag{5}$$

Because of the fourth term on the right hand side of eq. (7), $\epsilon_{\rm QW}(n, \mathbf{k}_{\parallel})$ is no longer the constant for \mathbf{k}_{\parallel} and the divergence of $D(\epsilon_{\rm F})$ does not occur often, even when $k_z(n, \mathbf{k}_{\rm F\parallel})$ matches $k_{\rm Fz}$ and eq. (6) is satisfied. Furthermore, the divergence of $D(\epsilon_{\rm F})$ can be promoted if we appropriately modify the \mathbf{k}_{\parallel} -dependence of Φ even when $k_z(n, \mathbf{k}_{\rm F\parallel})$ does not match $k_{\rm Fz}$ or eq. (6) is not satisfied. Thus, we can expect that a fine control of the \mathbf{k}_{\parallel} -dependence of phase shift Φ can reduce the magnetism in a similar way to induce the magnetism for nonmagnetic materials.

In the case of quantum confinement of Pd $d_{xz,yz}$ electrons, which we discussed in this paper, the hybridization between the *d*-electron wave function of the stacking layer and Pd at the zone edge (S-point) is intrinsically important for producing a flat band. Because typical 3, 4, 5*d* transition metals forming fcc structure have *d*-electron bands around the S-point, this effect generally occurs by stacking of these

transition metals on Pd(100) films. In addition, if the *d*-electron band of a stacking layer appears near the Fermi energy at S-point, magnetic change via modifying phase shift might be clearly observed, as indicated in eq. (5).

The present DFT calculation using Phase/0 code [2] well verified the above theory [1]. The electronic states of Au stacked Pd film were modified by changing the Au-Pd layer distance, and the QW induced ferromagnetism was controlled. Contrastingly, we observed that stacking of Al, which contains only selectrons around Fermi energy, cannot modify the shape of the band dispersion of delectron QWs because there is no hybridization between the s- and d-electrons. We see above behaviour from the calculated band dispersion and the shape of wave function. Our findings suggest a mechanism for controlling magnetism using modification of interface electronic states in metal-nano structures.

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Stability of vacancy cluster and interaction with impurities in tungsten lattice

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Introduction

The study of lattice defects in tungsten (W) are important issue in the field of fusion reactor because W is one of the plausible plasma facing materials (PFMs). Usually, hydrogen (H) and H isotopes seldom dissolve in W. However, H atoms are trapped in the vacancy-type lattice defects (vacancy clusters etc.) created in the irradiation circumstance. In particular, tritium (T) retention in the PFM is one of the serious problem associated with fusion reactor because T is radioisotope whose half-life is 12 years. So, the stability and binding energy of the vacancy clusters in the bulk W were investigated by simulations and experiments.

Small vacancy clusters in the W lattice has been reported to be unstable by the firstprinciple calculations. On the other hand, such small clusters and their growth to larger clusters were observed in positron annihilation lifetime measurements. In the present work, we investigate the reason why the small vacancy clusters exist in the W lattice. The vacancy clusters are stabilized by impurities. In particular, they are greatly stabilized by the presence of oxygen.

Simulation method

The binding energies of the vacancy clusters were calculated in terms of first-principle calculations based on density functional theory. We used the Vienna ab-initio simulation package (VASP). A large simulation cell, composed of 6x6x6 bcc lattice (432 atoms), were used in order to reduce the effects of periodic boundary condition imposed on the simulation cell. The cut-off energy of plane wave was 520eV.

The binding energy of vacancy cluster composed of n mono-vacancies V_n was defined

 $E_b(\mathbf{V}_n) = nE[\mathbf{V}] - \{E[\mathbf{V}_n] + (n-1)E[\mathbf{P}]\},\$

where *E* is cohesive energy of the supercell and P indicates perfect lattice of W. Positive binding energy corresponds to attractive interaction. Similarly, the binding energy of vacancy cluster containing an oxygen V_nO is

$$E_b(\mathbf{V}_n\mathbf{O}) = E[\mathbf{V}_0] + (n-1)E[\mathbf{V}] - \{E[\mathbf{V}_n\mathbf{O}] + (n-1)E[\mathbf{P}]\}.$$

Results

We investigated the most stable structure of vacancy clusters composed of *n* mono-vacancies without and with an oxygen ($n \le 6$). We examined di-vacancy V₂ in the first (1nn),

second (2nn), and third (3nn) nearest neighbor configurations. The di-vacancy in the 1nn configuration is the most stable among them. However, small vacancy clusters, V₂ and V₃, are energetically unstable compared with isolated mono-vacancies, as shown in Fig. 1. On the other hand, larger vacancy clusters, V_n ($n \ge 4$), are stable. Therefore, if V₄ were nucleated in the bulk W, the vacancy cluster growth would spontaneously occur.

The presence of impurities in W lattice contributes to the stabilization of vacancy clusters. Fig. 2 shows the most stable structure of vacancy clusters with an oxygen V_nO . The most stable structure of V_2O is the 2nn configuration, which is different from that without an oxygen V_2 . According to Fig. 1, all vacancy clusters trapping an oxygen are stable and the binding energy increases as a function of the number of vacancies composed of the vacancy clusters.



Fig. 1: Binding energies of vacancy clusters without and with an oxygen, $(V_n \text{ and } V_n O)$.

Discussion

Growth of vacancy cluster in W lattice was observed in the positron annihilation lifetime measurements but the vacancy clusters were expected to be energetically unstable in the firstprinciple calculations. We examined the stabilization effects by impurities contained in the W specimen. Even if high purity metal specimen were prepared, some kinds of impurities would be inevitably contained. Carbon, nitrogen, and oxygen are the typical inevitable impurities in the actual metals. Actually, vacancy clusters are greatly stabilized by the presence of such impurities. Besides, the diffusivity and binding energy to a monovacancy of oxygen in the W lattice are remarkably larger, compared with other impurities. The presence of oxygen is the most plausible candidate to explain the vacancy cluster growth observed in the positron annihilation lifetime measurements.



Fig. 2: Schematic view of the most stable structure of vacancy clusters trapping an oxygen (V_nO). The doted circles indicate positions of mono-vacancies in bcc W lattice.

First principles study on static structure of glass materials

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Cu₂GeTe₃ (CGT) is one of fast phase transition materials. This material changes between crystalline and amorphous phases quickly like Ge₂Sb₂Te₅. In order to clarify the phase transition mechanism, many experimental and theoretical studies were carried out so far. From results of anomalous xray scattering and extended x-ray absorption fine structure experiments, the local and intermediate range structures of glass were preserved structural motifs of the crystal [1]. However, the ring structure from theoretical study [2] was different from the experimental result [1]. In order to clarify the structure of amorphous CGT, we have performed ab initio molecular dynamics simulations.

In this study, we made two amorphous states, which were called a1 and a2 amorphous states. Figures 1 shows the distribution of number of *M*-membered ring P(M) [3]. In the crystalline state, there are only six-membered rings. In the amorphous state, some sixmembered rings are distorted from 6 to 3+5 rings, and distorted six-membered rings also remain in the amorphous state [1]. Using ring analysis method for our *ab initio* molecular dynamics simulations, the similar distribution

of number of ring to that from the experiment [1] was obtained [3]. This result shows that the distribution of six-membered ring is higher than that by Chen *et al.* [2]. The coexistence of 3+5 and distorted 6 membered rings would enhance the fast phase transition between crystal and amorphous phases.

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Fig. 1 The distribution of number of *M*-membered ring P(M) [3].

Graphene-based Symmetric and Non-Symmetric Magnetoresistive Junctions

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We have studied the structural, magnetic, and spin-dependent transport properties of Graphene based MTJs using massive parallel computer simulations. Gr layer is sandwiched between ferromagnetic electrodes.



Typical Dirac cone feature of Gr is not preserved upon the formation of MTJ and Gr derived π states near the Fermi level was strongly hybridized with the dz^2 orbital of the Ni and Co surfaces. APC was found to be stable in the Grbased ML junctions and distinct hybridization of the Gr π states are observed with symmetric and non-symmetric junctions. Spin filtering is quite sensitive to the electrode materials. The symmetric junction has higher TMR ratio compared to non-symmetric junction.

The highest TMR ratio observed in symmetric junction is 13.60%, while it is 8.26% in non-symmetric Gr based junction. Gr based junctions displayed the higher transmission spectra indicating low contact resistance irrespective of the electrode material.



Furthermore, the influence of different stacking of electrode layers on transport properties is also checked although not much difference is observed in conductance spectra. Both symmetric and non-symmetric junctions exhibit distinctive selection rules due to the incompatibility of wave functions of electrodes. Our comparative study reveals the effect of various electrode materials on spin transport property that can help to develop Gr-based high TMR ratio devices.

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Local physical quantities analysis based on the quantum field theory in material surface

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The local physical quantities, which is defined in the framework of quantum field theory (energy-momentum tensor density, current density, chiral current density, and so on), are significant to understand the fundamental aspect of nature of materials. In particular, since surface materials and two dimensional materials may have physical or chemical properties which cannot be explained by bulk feature in solids, it is important not only to evaluate the energy of the whole system and band structures but also to investigate the local physical properties.

In the previous work, the local physical quantities in molecular systems have been investigated by using a post-process calculation from wave packets obtained by molecular orbital method [1].

In this project, we developed a program code which enables us to calculate local physical quantities as a post-process calculation from OpenMX [2] (DFT calculation program code) in order to evaluate the local physical quantities in large periodic systems. It supports OpenMP/MPI parallelization to handle large system calculations.

The physical and chemical nature around the interaction region between a $\sqrt{7} \times \sqrt{7}$ Si(111) surface and a Si cluster (a model of atomic force microscopy tip), were investigated as a demonstration. The system is a periodic system including 402 atoms in a unit cell. The Fig. 1 shows that the maximum eigenvalues of the electronic stress tensor density around the region between the surface and the Si tip are positive (tensile stress) and the eigenvectors form the spindle structure [1], which visualizes a covalent bonding. In the future work, more detail analysis will give a deep understanding of chemical bond formation between a material surface and a molecular cluster.



Figure 1: Distribution of maximum eigenvalues and eigenvectors of the electronic stress tensor density and zero surface of the electronic kinetic energy density in the region between Si tip and $\sqrt{7} \times \sqrt{7}$ Si(111) surface.

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First principle simulation on reactions and electronic structures of new material synthesized from organic molecules

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We have experimentally synthesized new carbon materials by applying high temperature and / or high pressure to organic molecules. Using this ISSP supercomputer time, we have studied the reactions and electronic structures of these materials[1-3]. We present some of the examples.

Figure 1 shows optimized structure of graphitic carbon nitride $(g-C_3N_4)$ and a nitrogen molecule. We developed a liquid nitrogen based quenching process to prepare photocatalyst materials with atomic layer separated. This process greatly improved the photocaltalytic activity of the material. This calculation supports N₂ molecule can be intercalated to g-C₃N₄, which assists exfoliation of the layers.



Fig. 1: Optimized crystal structure of twolayered g- C_3N_4 and N_2 -inserted interlayer of g- C_3N_4 .

Figure 2 shows optimized structure of dibenzo[a,c]dibenzo[5,6:7,8]quinoxalino[2,3-

i]phenazine (DDQP) under pressure[4]. It shows Diels-Alder type intermolecular reaction. The electronic band structures showed threedimensional dispersion (Fig.3).



Fig. 2: Pressure-induced bond formation reaction of DDQP revealed by calculation.



Fig.3 Band dispersion of pressure-polymerized DDQP.

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Developments of a derivation method of a low-energy models in first-principles

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First principles calculation is useful method to determine the electronic structure. Most of the first-principles assumes local density approximation(LDA) in density functional theory, however, LDA usually underestimates band gaps of semiconductor. This underestimation is overcome by the consideration of the effect of particle excitation. The quasiparticle self-consistent GW method (QSGW) is a firstprinciples method to determine the one-body Hamiltonian H_0 taking into such excitation effects account.

However, even QSGW improves the size of band gaps compared to LDA, there still have some errors. For example, QSGW systematically overestimates the size of band gaps [1]. This overestimation is investigated from the viewpoint of vertex correction on the proper polarization P by Shishkin *et al.*. Their work has shown that such vertex corrections improve the dielectric constant very well. However, their method is somewhat ambiguous and consuming for computing resource.

To solve this problem, we introduced a method to numerically estimate the vertex correction[3]. Our method is to determine the vertex correction by a self-consistent calculation applying static electric fields to obtain the linear response of electronic density. On this purpose, we implemented the combination of QSGW and effective screening medium method (ESM, Ref. [4]). Namely, we calculate a slab model applying an external electrostatic potential varying along z axis. Fig. 1 is a schematic picture of ESM method applied to MgO slab. Then, it is better that slabs are as thick as possible because we intend to estimate the vertex correction of bulk materials.

To access the effectiveness of our method, we calculate optical dielectric constant ϵ_{∞} , where ϵ_{∞} is measured by the slope of the electrostatic potential. In Tab.1, we compare ϵ_{∞} of bulk calculation in the random phase approximation (RPA) and the QSGW+ESM method. Here we applied generalized gradient approximation(GGA) instead of LDA. We have chosen five simple ionic materials LF, KF, NaCl, MgO, and CaO for the examination system. We can find that QSGW+ESM is in an extremely good agreement with experiments. It is interesting that LDA(GGA)+ESM method does not necessarily improve the value of ϵ_{∞} . This may because that the exchange effect taken in the exchange correlation functional of GGA is not accurate.

In Tab.1, the underestimation of ϵ_{∞} of bulk system corresponds to the overestimation of band gaps. It is also found that the material dependence of the vertex corrections is not so large. From this result, some hybrid methods between QSGW and GGA may be applicable instead of present QSGW+ESM method as a compromise. In the previous work by Deguchi *et al.*, a hybrid method named QSGW80 (hybridization between QSGW and GGA at the ratio 8:2) has shown good agreements with experiments. Therefore, the systematic overestimation of QSGW may be improved by considering vertex corrections, which are effectively taken into account in QSGW80.



Figure 1: Schematic picture of ESM method. The upper panel shows the electrostatic potential when the difference bias voltages at z = 30, -30 are 0.0 Ry and 0.2, respectively. The lower panel shows the difference between the potentials among these to cases. The optical dielectric constant ϵ_{∞} is measured from the ratio of the slope between vacuum and slab region, as indicated in the lower panel.

To summarize, we have developed QSGW+ESM method to determine the vertex correction in QSGW. Our method can calculate dielectric function in a good agreement with experimental observation. The future problem is to derive a low-energy model Hamiltonian based on the one-body Hamiltonian H_0 derived from QSGW or QSGW80.

Table 1: Calculated optical dielectric constant ϵ_{∞} . 'RPA' are in bulk calculations. 'Slab' are calculated from the slab models in the setting of Fig.1.

		RPA	Slab	Experiments
LiF	GGA	1.95	2.01	1.06
	QSGW	1.67	1.94	1.90
KF	GGA	1.96	1.94	1.85
	QSGW	1.68	1.86	1.05
NaCl	GGA	2.33	2.42	9.34
	QSGW	1.92	2.31	2.04
MgO	GGA	2.96	3.09	2.06
	QSGW	2.50	2.37	2:91
CaO	GGA	3.59	3.68	2 22
	QSGW	2.88	2.68	3.31

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First-principles calculation of

the higher-order phonon-phonon scattering strength

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Phonon-phonon interaction is a key parameter that describes thermal transport properties in solids [*e.g.*, 1]. First-principles calculation of lifetimes of phonon quasiparticles owing to the interaction is computationally demanding for precise determination of phonon thermal conductivity. From the theoretical point of view for the many-body interacting systems, the phonon-phonon scattering rate is approximately inversely proportional to the imaginary part of the phonon self-energy [1]. Most density-functional theoretic calculations for determining phonon thermal conductivity is limited to the lowest order phonon-phonon interaction. The higher-order anharmonicity is likely to contribute to the conductivity particularly at temperatures higher than the Debye temperature as would be seen in the deep Earth's interior [2]. The primary purpose of this project in this period is to try to establish a roadmap as a first step for the accurate determination of phonon thermal conductivity at high temperature considering the effect of higher-order phonon-phonon scattering. Silicon was selected for this purpose for its simplicity.

We have performed the density-functional theoretic calculations based on the plane-wave basis pseudopotential method within the local density approximation. In order to extract harmonic and anharmonic force constants (AFC), the higher-order derivatives of the adiabatic potential surface were determined by the self-consistent field calculations for the structures in which some atoms are slightly shifted from the equilibrium positions. The $3\times3\times3$ cubic supercell containing 216 atoms in total was primarily adopted in this study to capture the anharmonic interaction.

During this period, by the use of supercomputer (system B) in ISSP, we have launched test calculations to check the computational conditions regarding the size dependency in the AFC, convergency in the with respect to the simulation cell size of the mesh to sample the phonon wave number vectors. Also, the self-consistent field calculations to extract AFC using the optimum condition have been almost finished. In parallel, post-processors to calculate the total phonon-phonon scattering rate including up to the fourth-order anharmonicity and thermal conductivity based on the Boltzmann transport equation have been almost developed. Using the complete data set

obtained in this study, we will make a thorough examination of the effect of the higher-order scattering on the lattice thermal conductivity at high temperatures. After the establishment of the procedure to compute the thermal conductivity, we plan the application of the developed technique to Earth's minerals under very high-temperature conditions [2].

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Theoretical Study on the Aggregation-Induced Emission

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In this study, the mechanism of aggregationinduced emission (AIE) of diphenyldibenzofulvene (DPDBF) was studied theoretically.

The DPDBF has been known to exhibit the AIE, which is non-emissive in dilute solutions but becomes highly emissive in solid or aggregates [1]. In this study, the AIE of DPDBF was investigated by using *ab initio* electronic structure calculations, together with molecular dynamics (MD) simulations.

In order to elucidate the characteristics of the potential energy profiles for the photochemical processes of DPDBF, the minimum energy paths for the photo relaxation process of DPDBF in an isolated phase were investigated using ab initio electronic structure calculations. The spin-flip approach within the time-dependent density functional theory (SF-TDDFT) method was used to compute the potential energies and analytical gradients for the electronic ground (S_0) and first excited (S_1) states of the molecule. All electronic structure calculations of DPDBF presented herein were performed using the GAMESS program.

The results of SF-TDDFT calculations showed that the potential energies of DPDBF for electronic ground (S₀) and first excited (S₁) states are degenerated at a conformation with the twist angle of 90° around its ethylenic C=C bond, which can lead the fluorescence quenching of DPDBF molecule in dilute solutions.

The free-energy profile of the photo isomerization of DPDBF in condensed phase was computed using MD simulations based on an empirical force field representation. All MD simulations of DPDBF presented herein were carried out using the GROMACS program.

The results of MD simulations revealed that DPDBF tends to assemble in close contact, where the ethylenic C=C bond rotation is markedly restricted in aggregates, preventing the fluorescence quenching via the S_0/S_1 conical intersection; DPDBF in acetonitrile solution, however, proceeds a barrierless nonradiative transition. These results gave a clear picture of the AIE of DPDBF, which is agree with that of a cyanostilbene derivative [2].

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Benchmark of density functional theory for superconductors in elemental materials

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1 introduction

The first-principles calculation of the superconducting properties, such as the transition temperature (T_c) and the gap function, is of great interest to explore new materials as well as to understand the physical mechanism of known superconductors. Density functional theory for superconductors (SCDFT) is one of the frameworks for such calculations; this method enables us to perform fully non-empirical simulations in the superconducting phases at a reasonable computational cost. In SCDFT, we can treat the electronphonon interaction, the electron-electron repulsion, the spin-orbit interaction (SOI) [1], and the spin-fluctuation (SF)-mediated interaction in a first-principles manner.

However, the accuracy of the current approximated functional of SCDFT and the effects of SOI and SF have not been verified systematically, although such verification is highly desirable before applying this method to a wide range of materials. Such a highthroughput calculation was performed, for example, in the exploration of low-thermalconductivity compounds using first-principles calculations together with the materials informatics. A benchmark is also a useful tool used to find a guideline for improving the theory and approximations of the superconducting density functional. For this purpose, in this project, we are presenting the benchmark calculations of SCDFT [2]. As benchmark targets, we have chosen the simplest superconducting, and nonsuperconducting materials, i.e., elemental materials; each material in this group comprises a single element. The particular computational cost is relatively low because most materials in this group contain only one or two atoms in the unit cell. Moreover, we can see the effects of the chemical difference and the strength of the SOI of each element.

2 method

Within SCDFT, T_c is obtained as a temperature where the following Kohn-Sham superconducting gap $\Delta_{n\mathbf{k}}$ becomes zero at all the band n and wavenumber \mathbf{k} :

$$\Delta_{n\mathbf{k}} = -\frac{1}{2} \sum_{n'\mathbf{k}'} \frac{K_{n\mathbf{k}n'\mathbf{k}'}(\xi_{n\mathbf{k}},\xi_{n'\mathbf{k}'})}{1+Z_{n\mathbf{k}}(\xi_{n\mathbf{k}})} \times \frac{\Delta_{n'\mathbf{k}'}}{\sqrt{\xi_{n'\mathbf{k}'}^2 + \Delta_{n'\mathbf{k}'}^2}} \tanh\left(\frac{\sqrt{\xi_{n'\mathbf{k}'}^2 + \Delta_{n'\mathbf{k}'}^2}}{2T}\right),$$
(1)

where $\xi_{n\mathbf{k}}$ is the Kohn-Sham eigenvalue measured from the Fermi level ($\varepsilon_{\rm F}$) at the band index *n* and wave-number \mathbf{k} . $\xi_{n\mathbf{k}}$ is obtained by solving the spinor Kohn-Sham equation. The integration kernel $K_{n\mathbf{k}n'\mathbf{k}'}(\xi,\xi')$ indicates the superconducting-pair breaking and creating interaction and comprises the following three terms:

$$K_{n\mathbf{k}n'\mathbf{k}'}(\xi,\xi') \equiv K_{n\mathbf{k}n'\mathbf{k}'}^{ep}(\xi,\xi') + K_{n\mathbf{k}n'\mathbf{k}'}^{ee}(\xi,\xi') + K_{n\mathbf{k}n'\mathbf{k}'}^{sf}(\xi,\xi'), \qquad (2)$$

namely, the electron-phonon, Coulomb repulsion, and spin-fluctuation kernel, respectively. However, the renormalization factor $Z_{n\mathbf{k}}(\xi_{n\mathbf{k}})$ comprises only the electron-phonon and spinfluctuation terms as follows.

$$Z_{n\mathbf{k}}(\xi) \equiv Z_{n\mathbf{k}}^{ep}(\xi) + Z_{n\mathbf{k}}^{sf}(\xi), \qquad (3)$$

because the Coulomb-repulsion contribution to this factor is already included in the Kohn-Sham eigenvalue $\xi_{n\mathbf{k}}$.

3 Result and Discussion

We have plotted $_{\mathrm{the}}$ computedand experimental- T_c in Fig. 1 to visualize the effect by SOI and SF; we can detect the following trends by inspecting this graph: SF always reduces T_c s for the elemental systems. This reduction becomes significant for the transition metals and is crucial to reproduce the experimental T_c quantitatively. In the transition metals, the effect of SF weakens with the increasing of the period number in the periodic table. The effect of SOI is small in most cases, excepting Tc, Sn, Re, In these elements, the Fröhlich's Tl, Pb. parameter λ changes drastically by turning on the SOI. We can reproduce the absence of the superconductivity in alkaline, alkaline earth, and noble metals, excepting Pt and Au with SOI and SF; we have observed small finite T_c for these two elements; we can reproduce the non-superconductivity also in Sc by including SF while we observe $T_c = 2.711$ K by ignoring SF. Since Sc has highly localized 3d electrons, the SF largely reduces T_c . For the group 12 elements (Zn and Cd), T_c s are overestimated even if we include SF. For these materials, the SF effect is small because the d orbitals are fully occupied.

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Figure 1: Theoretical and experimental T_cs [2]. The vertical axis is the atomic symbol together with the group of the periodic table. Downward (upward) triangles indicate the T_cs computed with (without) SF. Filled (empty) triangles indicate the T_cs computed with (without) SOI. "+" indicates the experimental value of T_c . The plot which ranges from zero to two Kelvin in the upper panel is magnified into the bottom panel.

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Simulation of scanning tunneling microscopy images of graphene ribbons with edges

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We are aiming at elucidating local electronic structures of finite-size graphene sheets and their impact on scanning tunneling microscopy (STM) images. For this purpose, we have started firstprinciples calculations of single-layer graphene ribbons possessing either zigzag or armchair edges by the use of a simulation package named STATE (Simulation Tool for Atom TEchnology).



Fig. 1(a) Structure of single-layer graphene



Fig. 1(b) Simulated STM image of single-layer graphene

STATE is based on the density functional theory. The exchange and correlation potential is described by the generalized gradient approximation by Perdew-Burke-Ernzerhof (GGA-PBE). We also used both a plane-wave basis set and pseudopotentials. When running STATE, we first defined the atomic structure of a finite-size graphene. This model as well as other parameters were placed as an input file on a supercomputer. The self-consistent field method was employed, which is an iterative method that involves selecting a Hamiltonian, solving the Kohn-Sham equation to obtain a more accurate set of orbitals, constructing the potential for each wave function, and solving the Kohn-Sham equation again with these until the results converge. In order to draw a map of local density of states, an electron density was integrated over an energy window of 0.05 eV below the HOMO (Highest Occupied Molecular Orbital). At each (x, y) coordinate, a z-height possessing the same electron density (1×10^{-4}) /Bohr³) was investigated and its contour map was depicted, which is regarded as a simulated STM image at the sample bias of -0.05 V. We

used the module (intel/18.0.5.274) for the compilers and mpt/2.16 for MPI library. The set of calculation was usually executed on F4cpu or F36cpu with suitable nodes in ISSP.

To check both the validity of our parameters in the input file for STATE calculations and the performance of STATE itself, we first modeled an infinite, single-layer graphene. The created model is shown in Fig.1(a). The cutoff energies were 36 Ry (GMAX=6) and 400 Ry (GMAXP=20) for the wave functions and the augmentation charge, respectively. Then we conducted first-principles calculations within STATE to get the electronic structure of the model. Figure 1(b) shows a simulated STM image of the surface in Fig. 1(a) at the sample bias of -0.05V. A brighter area in Fig.1(b) indicates a higher corrugation, which is caused by a higher density of the occupied states. It is apparent that a hexagonal pattern is formed in which the position of a bright dot coincides with that of a carbon atom comprising the graphene network. Figure 1 insists that the combination of our modeling and parameters with the STATE software works well. In the next fiscal year, we are going to characterize the distribution of local charge densities near the edges of a graphene ribbon and to unveil its relationship with an STM image around the Fermi level.

An open source code for QUANTUM ESPRESSO to compute irreducible representations of Bloch wave functions

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Since the remarkable discovery of \mathbb{Z}_2 topological insulators, topological materials have attracted researchers around the world. Topological materials host robust surface states and exhibit unique bulk responses, which could be leveraged for new low-power devices. Therefore, discovering various topological materials is one of the important tasks for engineering.

Given a symmetry setting, establishing topological invariants that characterize all possible topological phases is a pending problem. Furthermore, it is sometimes difficult to compute topological invariants even when we know the mathematical definition of topological invariants. However, when spatial symmetries exist, it is effortless to diagnose topological phases by using information of spatial symmetries. A prototypical example of this relation is the Fu-Kane formula, which can evaluate the topological invariant of insulators from eigenvalues of the inversion symmetry. In recent years, this idea has been generalized to all combinations of crystalline symmetries by using irreducible representations of wave functions instead of eigenvalues, and the generalized theory is called symmetry indicators [1]. While it does not bring the complete classification, this theory is suitable to discover realistic topological materials. In fact, this method is a basis of recent comprehensive surveys of topological materials among existing databases of inorganic substances. As a result, thousands of candidates of topological (crystalline) insulators and semimetals have been discovered. In addition to these developments, the theory of symmetry

indicators has been extended to magnetic space groups and superconductors [2].

As seen in the preceding paragraphs, it is helpful to compute irreducible representations by using DFT. Although the authors of Refs. [3,4] implemented programs for WIEN2k and VASP to calculate irreducible representations, these packages need paid licenses. In contrast, QUANTUM ESPRESSO, a free package for ab initio calculations, can obtain irreducible representations only for symmorphic space groups.

In this work, we developed an open-source code for QUANTUM ESPRESSO to get irreducible representations for all space groups. In addition to this function, we implemented a function to automatically compute the \mathbb{Z}_4 index that can diagnose various topological phases such as higher-order topological insulators. Furthermore, we also apply our program to about 40 magnetic materials. Then, we used the facilities of the Supercomputer Center to get wave functions for these materials. We are still searching for new topological materials by using our program and DFT calculations.

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First Principles Calculation of 2-Dimensional Silicides Formed on Nickel Surfaces

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Metal silicides are indispensable materials for advanced microelectronics. We have recently proposed a new route to form a robust two-dimensional (2-D) silicide [1,2]. Unlike conventional thin film silicide formed by depositing metal on the silicon surface, Si was deposited on a clean metal surface to form silicide. Our recent studies show that robust 2-D silicides are formed on Ni(110) and Ni(100) surfaces due to the large diffusion asymmetry between Si in bulk metal and metals in bulk Si [1,2]. However, the lack of theoretical support clearly undermines the significance of our research findings.

First-principles calculation code VASP was adopted to compare the experimentally obtained 2-D atomic structure with theoretical simulations. A typical scanning tunneling microscope (STM) image of a Si-deposited Ni(100) surface is shown in Fig. 1 [2]. The initial clean surface was essentially a 1×1 structure, but many dark sites were formed after Si deposition. These dark sites are not due to structural defects, but Si replaced by Ni in the



Fig. 1 Typical STM image for a 0.39 ML Si deposited surface. White square corresponds to the 1×1 unit cell. top layer. Since the STM image is reflected by the surface local density of states (LDOS) near E_F , the embedded Si reduces the tunneling current without the large LDOS due to Ni 3*d* bands, making it a dark site. Therefore, the discrimination between individual Si and Ni is fairly straightforward, but the relationship between Si and Ni is unsolved.

Therefore, the first principle calculation was performed in this system. The calculation parameters are shown in Table 1. Before performing surface slab calculations, we evaluated the ground state energies of Ni and Si atoms, and bulk Ni and Si, respectively. Because of the slow convergence of selfconsistent electronic states in the surface structure, we adjusted the mixing parameters as shown in Table 1 (so-called linear mixing, see VASP manual). First, all atoms except for the middle layer has been completely relaxed. Then 0-8 surface Ni atoms in the top layer were replaced by Si, and the top 5 layers were fully optimized. A total of 36 different surface configurations were evaluated for 0-1 ML Si coverage.

In order to compare the formation energy for different numbers of surface species, we evaluated chemical potential as,

$$E_{total} = E_{slab} - n_{Ni} E_b^{Ni} - n_{Si} E_b^{Si},$$

where E_{slab} is a total energy of a particular slab structure, n_{Ni} and n_{Si} are respectively numbers of Ni and Si atoms in the slab, and E_b^{Ni} and E_b^{Si} are respectively bulk cohesive energies for Ni and Si.

As shown in Fig. 2, the relative energies of various configurations referenced from that for the Ni(100) surface are plotted as a function of Si coverage. Negative formation energy means that energies of Si embedded structures are lower than that of the Ni(100). There is a negative slope for Si coverage from 0 to 0.5 ML, indicating that Si substitution with Ni is energetically favorable. On the other hand, a positive slope above 0.5 ML means that Si will be ejected from the structure, which is in good agreement with experimental observations.

In conclusion, the first-principles study of two-dimensional Ni silicide formed on Ni (100) is in good agreement with the experimental

Table 1 Parameters for present calculation

	•		
VASP Version	5.3.5		
slab geometry	Ni(100) 2×4 unit		
	11 layers		
vacuum region	2.12 nm		
k-points	16×8×1		
potential	PBE [3]		
cut off energy	350.39 eV		
Fermi level smearing	Methfessel & Paxton		
-	$\sigma = 0.12 \text{ eV}$		
convergent condition			
ion cordination	0.01 eV/Ang.		
electronic states	$10^{-5} \mathrm{eV}$		
mixing parameters	spin-resolved		
	AMI = 0.02		
	BMIX = 0.0001		
	$AMIX_MAG = 0.08$		
	$BMIX_MAG = 0.0001$		
0.2			



Fig. 2 Relative formation energies of Si-embedded Ni(100) surfaces with various configurations of Si coverage between 0-1 ML. Inset: The most stable configurations with Si coverage of 0.125, 0.25, 0.375, and 0.5 ML.

results. As a future study, the displacement process, so-called depressive adsorption, should be revealed by molecular dynamics simulations.

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First-principles Study of Defects of Magnesium Alloys

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Magnesium (Mg) has been of increasingly interest from the engineering viewpoint, because of its low density and relatively high specific strength. Despite intensive research efforts, there remain various problems to be overcome; low ductility and low toughness at room temperature. To understand active deformation mode under an applied load, the Schmid factor and the critical resolved shear stress (CRSS) for each deformation mode are helpful. However, several studies showed that the activated deformation mode under various uniaxial loadings deviated the Schmid's law and their CRSSs were not uniquely determined. In order to investigate influences of non-glide stress on deformation modes, we carried out molecular dynamics (MD) simulations for slips with <a> Burgers vector under several normal stress conditions. For basal slip, extended dislocations were generated and glided on the basal planes, irrespective of the applied normal stress conditions. In MD simulations of shear deformation for first-pyramidal slip, distinct dislocation gliding was not observed and alternatively (10-11) twin was generated. For prismatic slip, deformation behavior depended on the applied normal stress as well as

interatomic potentials.

One way for improving the limited ductility of Mg at room temperature is to activate nonbasal slips. In particular, Mg-Y alloy has shown a significantly enhanced ductility. It has been suggested that the improvement of ductility was attributed to the reduction of the intrinsic I_1 stacking fault (SF) energy by Y addition. We investigated defect nucleation in the vicinity of a pre-existing intrinsic I₁ SF by MD simulations. While formation of (11-21) twin was observed under shear stress on (0001) along [11-20], <c+a> partial dislocations were generated with SFs for higher resolved shear stress for pyramidal slips. The dissociation reactions of the dislocations at the side ends of the I₁ SF were energetically evaluated, and it was implied that nucleation of the <c+a> dislocations on the first-pyramidal planes is more favorable than on the second-pyramidal planes.

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First-principles study of magnetoresistance ratios and magnetic anisotropy in magnetic tunnel junctions

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Magnetic tunnel junctions (MTJs), where an insulating tunnel barrier is sandwiched between two ferromagnetic electrodes, are the most practical spintronic devices. The MTJs have various applications such as nonvolatile magnetic random access memories (MRAMs) and many types of magnetic sensors including read heads of hard-disk drives. For these applications, we have several requirements in the physical properties of MTJs. In the present work, we studied such properties using the first-principles calculations.

The spinel oxides AB_2O_4 can be hopeful insulating tunnel barriers in MTJs. Among them, MgGa₂O₄ (MGO) has recently attracted attention because the MGO-based MTJs have low resistance-area products (*RA*) and high magnetoresistance (MR) ratios [1], both of which are necessary for MRAM and read-head applications. To understand the mechanism of such properties, we calculated *RA* and MR ratios in the Fe/MGO/Fe(001) MTJ by combining the density-functional theory (DFT) and the Landauer formula. As a result, a low *RA* (~0.5 $\Omega\mu$ m²) and a high MR ratio (~200%) were obtained when the thickness of the MGO barrier is around 10 Å, which is consistent with experiments. We found that the low RA is attributed to a small band gap in the MGO barrier. In addition, our detailed analysis of the electronic structure clarified that the obtained high MR ratio can be understood from the interfacial resonance effect [2].

As a second topic, we tried the calculation of MR ratios in unconventional (111)-oriented MTJs, which have not been examined well so far owing to the successful history in the (001)-oriented MTJs. By using the first-principles approach mentioned above, we calculated a MR ratio of Co/MgO/Co(111) and obtained a quite high value (>2000%). We found that such a high MR ratio also comes from the interfacial resonance effect [3].

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Study on Carrier Dynamics in Nano Scale Semiconductor Devices with Machine Learning

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We have studied a Machine Learning (ML) approach to make a model of electron transport process in nanostructures. The transmission coefficients timeand development of electron density in the nanostructures are computed by timedependent schrödinger equation to provide training and test datasets to the machine learning [1,2]. Calculations are performed on the motion of electron wave packets of different energies in a two-dimensional nanostructure under random impurity distribution.

We work on the creation of two types of predictive models; the transmission probability of electron wave packet from the impurity distribution; the impurity distribution from the image sequence of electron density distribution in the transmission process. By combining these predictive models, we expect to achieve a more efficient device design method with time-dependent calculation than ever before.

As the ML methods, a Random Forest (RF) and a Neural Network (NN) are employed for modeling the relationship between the impurity distributions and the transmission coefficients of electron. The mean absolute error is compared to each model. In both methods, it is found that the approach of capturing the impurity distribution as an image could build a better model than using simple impurity coordinates as input.

In addition, we investigate the predictive model for the impurity distribution from the image sequence of the time evolution of electron density as shown in Fig.1. Modeling by convolutional NN is performed, and the accuracy is compared when the image sequence is individually inputted, when the mean of the image sequence is inputted, and when the image sequence is inputted with a recurrent network.



Fig.1 Modeling the impurity distribution from the image sequence of the time evolution of electron density.

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Analysis of absorption spectra for caged compounds in aqueous solution

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Coumarin caged-luciferins, which can generate firefly luciferin ('luciferin' in this article) by UV photolytic reaction, would be useful to understand the firefly bioluminescence. We synthesized the new caged-luciferin (coumarin caged-luciferin) and obtained the absorption spectra for this caged-luciferin itself and irradiated caged-luciferin[1]. When we use this caged-luciferin for spectroscopic studies, we need the detail of electronic states of this molecule in aqueous solutions. In this year, we performed the density functional theory (DFT) calculations for coumarin cagedluciferin .

The polarized continuum model was used for the description of water solute molecules. All calculations were performed using the GAUSSIAN09 [2] program on system B and C of Super Computer Center in ISSP. The ground states for 40 equilibrium structures for coumarin caged-lucifein in aqueous solution were obtained. The time dependent DFT (TDDFT) calculations for these structures were poerformed to obtain the theoretical absorption spectra.

Figure 1 shows the experimental and theoretical absorption spectra of coumarin cagedluciferin. The experimental absorption spectrum of luciferin is also shown in Figure 1. The shape of the theoretical absorption spectrum of coumarin caged-luciferin is quite similar to that of experimental spectrum. We found that the peak near 384 nm of theoretical absorption spectrum corresponds to the absorption from the ground electronic state (S_0) to the first excited state (S_1) and that the peak near 339 nm corresponds to the absorptions from S_0 to the second (S_2) and third (S_3) excited state[3]. We also found that the characteristics of 339 nm peak in the theoretical absorption spectrum of coumarin caged luciferin is similar to that of the peak in the absorption spectrum of luciferin.



Figure 1: Absorption spectra for coumarin caged luciferin and luciferin[3]. Black solid line : Experimental absorption spectrum of coumarin caged luciferin, Red solid line: Theoretical absorption spectrum of coumarin caged luciferin, Black dashed line: Experimental absorption spectrum of luciferin, Orange dashed line: the component of absorption from S_0 to S_1 , Green dashed line: the components of absorptions from S_0 to S_2 and S_3 .
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Calculation of multication oxide surface properties for catalyst informatics

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Surface point defects of metal oxides, for instance O vacancies, have a dominant effect on heterogeneous catalysis. The Mars-Van Krevelen mechanism is one of the most frequently encountered catalytic process. In one example, O vacancies on a metal oxide catalyst surface act as reaction sites. The energy minimum required to remove O from a surface, which is denoted as the surface O vacancy formation energy (E_{Ovac}) , can be used to rationalize and predict catalytic performance in such a catalytic process. Calculation of E_{Ovac} requires a slab-and-vacuum model with sufficient spacing between O vacancies, hence some estimation of E_{Ovac} from less costly calculations, such as slab-and-vacuum model calculations with minimum cell size and even bulk calculations, will be effective in screening materials for a given purpose.

The E_{Ovac} of ZnM₂O₄, where M is one of Al, Ga, In, V, Cr, Mn, Fe, or Co, was calculated. These compounds take the normal spinel structure, and the (100), (110), and (111) surfaces were evaluated. The automated nonstoichiometric and nonpolar slab-and-model generation algorithm already by Hinuma et al. [1,2] was expanded to allow automatic derivation of models where the topmost and bottommost surfaces need to be reconstructed. which is the case in the normal spinel surfaces in this study [3]. The surface energy was smallest in the (100) surface in all systems, and E_{Ovac} was largest in the (100) surface in all systems except ZnCo₂O₄. The reactivity of a site is expected to be high if the site is unstable. In other words, a site with low E_{Ovac} is expected to have a higher reactivity and therefore can open up new capabilities in, for example, catalysis. The importance of finding unstable sites, which roughly translates to having a lower E_{Ovac} for surface O sites, that are expected to have lower surface energy was identified in this study. Needless to say, the surface must be proven to be experimentally accessible, which is a very important issue that need to be worked on.

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Study on physical properties of structural elementary excitations of semiconductor surfaces and interfaces

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Our project has been focused on physical properties of structural elementary excitations of semiconductor surface and interfaces. We have performed three topics in this year. One is the physical properties of SiO interstitials in SiO₂ at interface with Si [1, 2]. The second is the physical properties of oxygen vacancies (V_O) in SiO₂ at interface with Si. And the third is the physical properties of vacancies in a two-dimensional material MoSe₂. The calculations were performed based on the firstprinciples calculation. Program package VASP was employed for the first and the third topics, while program package PHASEO was employed for the second topic.

In the first topic, we focus on the role of SiO interstitials for the selfdiffusions in SiO₂ under compressive pressure. It is known that SiO interstitials are injected into the oxide when Si is thermally oxidized. In addition, for Si pillar oxidation, it is known that a large compressive pressure as high as 5 GPa is induced in the oxide. We have calculated the pressure effect for temperatures 3000, 4000, 5000, and 6000 K, and derived activation volumes as well as activation energies. We found that the SiO really acts as a unit for the diffusion mechanism. As the result, the pressure dependence of Si diffusion is largely affected by the SiO incorporation, while that of O diffusion is not much affected. [1, 2]

In the second topic, we focus on the strain effect on V_O diffusion in SiO₂. As described before, for the Si pillar oxidation, a large com-

pressive pressure is accumulated in SiO₂. We have calculated activation barriers as the function of modulated lattice constants. We have also checked crystal polymorph dependence for Quartz, Cristobalite, or Tridymite. As the results, we found that the barrier height increases with the Si density almost being independent of the polymorph type. The reason comes from the fact that the initial Si-Si distance at V_O controls the barrier height.

In the third topic, we focus on the supporting effect on vacancy formation in monolayer $MoSe_2$. The results are similar to our previous study on MoS_2 . We found that the supporting effect makes the charging more difficult because the reduced quantum confinement shrinks the band gap. The hetero-stacking also makes the charging more difficult because the type II band alignment also shrinks the band gap. These lead to the reduction of charging effect on the vacancy formation.

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Theoretical Study on Electronic Properties in New Nanoscale Surfaces and Interfaces

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In 2019 we theoretically studied electron transport properties through higher-order topological insulators. Higher-order topological insulators were recently proposed theoretically [1]. Higher-order topological insulators are materials that have topologically protected states in two or more lower spatial dimensions. There are several reports that higher-order topological insulators are experimentally observed [2, 3]. We calculated electrical conduction properties through topological edge states in a three dimensional crystal.

We used a tight-binding model of higherorder topological insulators given by Langbehn *et al.* [4]. This model is a three dimensional insulator and has one dimensional edge states protected by mirror symmetry. Transmission properties through the edge states are investigated. We consider a cubic structure of higherorder topological insulator. Two electrodes are attached to two corners of the cube. The electrodes are normal conductors. We solve scattering states of the Hamiltonian of the open system. Electrical conductance is calculated using the Landauer formalism.

We consider several different conditions of contact between the high-order topological insulator and electrodes. Calculated conductance depends strongly on contact conditions. Conductance increases with increasing the strength of the contact for weak strength of contact. But, it turns to decrease with further increase of the contact strength. There is a peak in conductance as a function of the contact strength. This result is due to a following reason.

The incident electrons are transmitted to another electrode or reflected to the incident elec-

trode with conserved or inverted spin. The reflection with conserved spin is dominant in the region of weak contact strength. The spinconserved reflection decreases with increasing the contact strength. The transmission to the other electrode increases in place of the decrease of conserved reflection. However, with further increase of the contact strength, the reflection with inverted spin increases and it becomes dominant. Accordingly, the transmission turns to decrease. This result means that there is moderate contact strength for hight transmission.

In addition to the study of electron transmission properties through the high-order topological insulators, we also developed the calculation method of spin and angle resolved photoelectron spectroscopy. We extended the method for obtaining time-reversed LEED states from the results of repeated-slab calculations. It became possible to treat general cases containing any number of bulk Bloch states by using the singular value decomposition.

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Development of First-principles calculations method of Seebeck coefficient in the framework of linear response theory

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The simulation of the Seebeck coefficient is mainly calculated by using the relaxation time approximation to the Boltzmann equation, but this approximation is correct only if the relaxation time is constant, and it is not a good approximation method for transition metal systems where the band structure on the Fermi surface is very complex. As a method to solve this problem and calculate the Seebeck coefficient in a non-semi-classical quantum mechanical way, a method to calculate the Seebeck coefficient from the energy dependence of electrical conductivity near the Fermi energy using linear response theory has been proposed. In this study, we deal with the temperature dependence of the phonon density of states and anharmonic oscillations, which are not considered in the method for obtaining Seebeck coefficients from electrical conductivities using linear response theory in previous studies.

The study combines three approaches: phonon density of state calculations, the CPA method for static phonons, and linear response theory in the framework of the KKR method. The electrical conductivity and Seebeck coefficients at finite temperature were calculated by using this method. Concretely, we first calculate the phonon density of states assuming harmonic oscillations by the direct method using the first-principles packages VASP[1] or Quantum-ESPRESSO[2] and ALAMODE[3] . Next, the average displacement of the atoms at each temperature is obtained from the phonon density of states, and the effect is incorporated into the Green function in AkaiKKR, which extends the CPA method to handle the effect of displacement. Finally, the Green function is substituted into the Kubo-Greenwood equation[4] of the KKR-CPA method by Butlar to calculate the temperature-dependent electrical conductivity, and the Seebeck coefficient is obtained from Mahan's equation [5]. In the transition metal system, which is considered to be difficult to calculate using the Boltzmann equation and the relaxation time approximation, we calculate the Seebeck coefficients for the simplest single transition metals using the above method, and confirm that the coefficients reproduce the experimental values well[6].



Figure 1: (Color online) Calculated (closed symbol) and experimental [7] (open symbol) Seebeck coefficients S of pure Cu, Mo, and W as functions of temperature.



Figure 2: (Color online) Calculated (closed symbol) and experimental[7] (open symbol) Seebeck coefficients S of pure Ag, Au, Pt, and Pd as functions of temperature.

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First-principles calculation of spin-density wave state in chromium metals

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Chromium metal films are one of practical materials for strain gauge sensor due to showing the high-sensitive response of the electrical resistivity by strain effect. [1] Though the mechanism of the high sensitivity is still unclear, we consider a possibility that the electrical resistivity of chromium metal is greatly influenced by lattice strain, through the modulation of the spin-density wave state. To verify this possibility in the theoretical view point, we analyze the strain effect on the electronic structure in the spin-density wave state of chromium metals by first-principles calculations. For the calculation of the incommensurate spin-density wave state in chromium metals, large unit cells including more than 40 atoms were adopted, with reference to the previous works by Hirai and Hafner *et al.* [2, 3]The Vienna ab-initio simulation package [4] was used for the calculations, where the exchange correlation functional was described within the general gradient approximation.

Figure 1 shows the calculation result of the total energy in the nonmagnetic (NM) state, the commensurate spin-density wave (CSDW) state, and the incommensurate spin-density wave (ISDW) state as a function of the lattice constant a. Note that the wave-number in the ISDW state was set to $q = 0.95 \cdot 2\pi/a$ [Å⁻¹]. The equilibrium lattice constant in the ISDW state is $a_{eq} = 2.845$ [Å], which is approximately 1% smaller than the experimental value $a_{exp} = 2.884$ [Å]. We should mention here that the ground state is not the ISDW state but



Figure 1: Total energy per atom in NM (red), CSDW (blue), and ISDW (green) states as a function of the lattice constant a.

the CSDW state in the calculation, however, the similar result was obtained in the previous works [2, 3]. On the other hand, it is remarkable that the magnetism of chromium metal disappears for $a \leq 2.78$ [Å]; this feature is qualitatively consistent with an experiment that the Néel temperature of metallic chromium becomes zero for applying 15 GPa of hydrostatic pressure. [5] This result implies that the magnetism of chromium metal is sensitively variable by lattice strain, corresponding to the fact that the magnetovolume effect is observed significantly in chromium metal.

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Development and application of the first-principles approach

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We have investigated unconventional superconductors in the strongly correlated electron systems (SCES). The main theme is to develop the first-principles calculations and well describe the electronic structure of SCES. This year, using a Class B, we have studied two topics; superconducting gap anisotropy of the layered Bismuth chalcogenide superconductors (Bi Ch_2) and the electron correlation effect of the gap structure in iron-based superconductors.

The layered $BiCh_2$ superconductors possess non-symmorphic structure. Locally inversion symmetry breaking and the strong spin-orbit coupling (SOC) on a Bismuth site can lead to the parity mixing between spin singlet and triplet pairing. In addition, the observed charge / orbital fluctuations potentially yield the gap anisotropy even without strong repulsive interactions. First, we performed the DFT band structure calculations using Qunatum espresso [1] in Sekirei system, and made an effective four-orbital models with the SOC using the maximum localized Wannier functions. We have solved the superconducting gap equation in multi-orbital attractive Hubbard model. In the obtained phase diagram, we have found a possibility of topological superconductivity. This study was reported in the JPS autumn meeting 2019 [2].

Next, in the iron-based superconductors, we have applied the quasi-particle self-consistent GW (QSGW) method to KFe₂As₂ and studied the gap structure in the effective Hubbard

model. In general, the conventional LDA / GGA calculations describe the overall feature of the band structure. However, the size and curvature of the Fermi surface and the composed orbital characters are significantly deviated from the experimental observations. This has a sizable effect on the gap structure. In Fig. 1, we indicates the Fermi surface and the gap structure. Emergence of propeller-type Fermi pockets is well consistent with the experimental data. Furthermore, the change of orbital characters turns the gap structure from horizontal nodes to octet node structure. This study was reported in MRM2019 [3].



Fig. 1 Gap structure on the Fermi surface in KFe₂As₂ obtained by GGA (left) and QSGW (right).

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